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# Characterization of MSW (Municipal Waste Combustion) Ashes and Leachates from MSW (Municipal Solid Waste) Landfills Monofills, and Co-Disposal Sites. Volume 5

NUS Corp., Pittsburgh, PA

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# Characterization of MWC Ashes and Leachates from MSW Landfills, Monofills, and Co-Disposal Sites

## Volume V of VII

## Characterization of Municipal Waste Combustor Residues

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# FINAL DRAFT

# CHARACTERIZATION OF MUNICIPAL WASTE COMBUSTOR RESIDUES

## VOLUME V OF VII

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Contract No. 68-03-3235
Delivery Order No. 3

# FINAL DRAFT REPORT CHARACTERIZATION OF MUNICIPAL WASTE COMBUSTOR RESIDUES

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# 1.0 INTRODUCTION

This report is the final deliverable for Delivery Order Number 3 of Contract 68-03-3235. The report (1) describes the planning, sampling and analysis activities; (2) summarizes the results of chemical analyses performed on fly ash, bottom ash, laboratory-prepared leachates of fly ash and bottom ash, field-collected quench water, leachate from mono-filled residue landfills, and ground water from monitoring wells located near the landfills; and (3) evaluates the results of analyses with respect to municipal waste combustor (MWC) facility design and operation, variations among leachate preparation procedures, and characterization of the residues as hazardous wastes.

The remainder of this section discusses the background of this contract, the objectives of the study conducted under Delivery Order No. 3, and briefly summarizes the technical approach taken in this study.

Section 2 presents the results of a limited review of published literature characterizing MWC residues.

Section 3 describes the approaches Versar took in selecting MWC facilities for sampling and analyses, describes the design and operational characteristics of the MWC facilities selected and their associated mono-filled landfills, describes the sampling procedures and samples collected at each MWC facility, and the sample handling and analysis procedures.

Section 4, presents and discusses the results of analyses of samples collected at the facilities by sample matrix (fly ash, bottom ash, laboratory-prepared leachate, quench water, landfill leachate, ground water) and by major constituent category (heavy metals, polychlorinated biphenyls (PCB's), polychlorinated dibenzo-dioxins and polychlorinated dibenzo-furans (PCDD/PCDF), and other organic constituents).

Subsection 4.5 discusses the results of internal and external quality assurance/quality control (QA/QC) procedures exercised on the analyses of the samples.

In Section 5 the data obtained in this project is analyzed and evaluated in several respects. In Subsection 5.1 the data is compared with selected data from the published literature and from other generally unpublished sources. In Subsection 5.2 comparisons are made between the concentrations of constituents measured in laboratory-prepared leachates (Extraction Procedure, Toxicity Characteristic Leaching Procedure, and the Mono-filled Waste Extraction Procedure) and concentration of constituents measured in field-collected water samples (quench water, field leachate and ground water). The objective of this comparative evaluation is to determine whether any of the extraction procedures currently required, or contemplated as being required in the future, for regulatory testing simulate actual environmental extraction processes. Subsection 5.3 provides a qualitative evaluation of the relationships observed in this study between MWC facility design and operating characteristics and the concentration of constituents observed in the residues. Subsection 5.4 provides an overall assessment of the hazardous waste characteristics of MWC residues.

The conclusions of this study are summarized in Section 6.

## 1.1 Background

This project was conducted under Delivery Order No. 3 of Contract 68-03-3235 administered through the U.S. EPA Hazardous Waste Engineering Research Laboratory, Cincinnati, Ohio. This contract was originally entitled "Evaluation of Site Characteristics Contributing to Pollution at Selected Hazardous Waste Disposal Sites".

Delivery Order No. 1 of this contract dealt with the selection of a limited number of hazardous waste disposal sites from several hundred existing sites nationwide for in-depth study of site and contaminant characteristics contributing to contaminant migration off-site. Delivery Order No. 1 was completed in July, 1985 with submittal of a final report detailing the approach used in evaluating and selecting candidate sites for in-depth investigation, and recommending five candidate sites, from which one would be selected.

Delivery Order No. 2 involved five Tasks: (1) establishing working relationships with the selected site owner/operator; (2) preparing a detailed work plan for investigations at the site; (3) acquiring existing site information; (4) conducting the investigation as planned, and (5) reporting the results of the investigation. Delivery Order No. 2 was completed through Task 3. Tasks 4 and 5 were cancelled due to changing priorities within the Agency and to potential conflicts that the proposed investigation might cause with ongoing litigation at the candidate sites selected.

Delivery Order No. 2 was amended in February, 1986 creating a new Task 4 calling for an evaluation of the effectiveness of lime/fly ash injection for stabilizing a typical solid waste landfill. Task 4 could not be completed because of unforeseen problems gaining access to landfills both privately and publicly owned for purposes of investigation. The results of the attempts to gain access to landfills were reported by letter in March and April, 1986.

Delivery Order No. 3 of this contract, issued in July, 1986, called for chemical characterization of residues from municipal waste combustor facilities. The title of the contract was changed to "Characterization of Municipal Waste Combustor Residues". The performance and findings of the study conducted under this delivery order are reported herein.

At the present time, the solid residues from MWC facilities are typically classified as non-hazardous and are placed in landfills regulated under Subtitle D of the Resource Conservation and Recovery Act (RCRA).

Studies on the solid residues conducted in the past few years, however, have shown the presence of heavy metals and organic compounds in concentrations of potential concern. Extraction Procedure (EP) Toxicity Tests performed on fly ash samples have shown that the concentrations of some metals (primarily cadmium , chromium and lead) in the EP leachate regularly exceed the maximum concentrations for the hazardous waste characteristic of EP Toxicity. In addition, polychlorinated dibenzo-dioxins (PCDDs), polychlorinated dibenzo-furans (PCDFs), and polychlorinated biphenyls (PCBs) have been found in the fly ash and flue gas from MWCs. PCDDs and PCDFs have been reported in fly ash samples from MWCs in the United States, Canada, Europe, and Japan.

The presence of some heavy metals in the EP leachate from fly ash at concentrations exceeding the regulatory limits, and the presence of potentially highly toxic organic compounds (PCDDs and PCDFs) in fly ash have raised questions concerning the proper disposal of MWC residues in general. Of special concern is the issue of whether MWC residues disposal is adequately regulated under Subtitle D of RCRA. In order to determine (1) whether an alternative regulatory strategy is needed for MWC residues and (2) the structure of an alternative regulatory strategy, scientifically-defensible data chemically characterizing MWC residues are needed.

The database presently available on chemical characterization, however, is limited in size and scope (chemicals tested for). Moreover, the available data have generally been obtained using inconsistent sampling techniques and analytical methodologies, and using uncertain or inadequate quality assurance/quality control procedures.

Work is underway under other EPA contracts to assemble information on MWC residues from other sources (state agencies, MWC facility operators, etc.), and initiatives have been submitted for chemical characterization studies during Fiscal Years 1987 and 1988. It is expected that neither of these efforts will provide the scientifically-defensible data needed for evaluation/development of alternative regulatory strategies by the end of Fiscal Year 1987 when the Agency is required to provide a preliminary report to Congress on this issue.

## 1.2 Objective

The objective of this project performed under this Delivery Order is to collect chemical characterization data on residues from municipal waste combustor (MWC) facilities. The residues characterized include fly ash from air emission control equipment, bottom ash, process quench water and leachate and/or ground water (when available) from mono-filled landfills containing the solid residues. In addition, ground water samples from any monitoring wells located near the landfills were to be characterized.

This project is intended to provide U.S. EPA's Office of Solid Waste with preliminary data characterizing MWC residues in advance of similar data to be provided in other studies underway or scheduled for initiation in Fiscal Years 1987 and 1988.

## 1.3 Summary of Approach

This study was conducted in five Tasks briefly summarized below:

### Task 1: Preparation of Work Plan and Quality Assurance Project Plan

The Work Plan was prepared in accordance with the Scope of Work and in consultation with the Project Officer, and approved August 15, 1986.

Following approval of the Work Plan, a Quality Assurance Project Plan (QAPP) was prepared in accordance with the guidance for Category II projects and with "Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans" (QAMS-005, December 29, 1980). The QAPP was approved with recommendations on October 8, 1986. During the course of the study, the QAPP was revised to respond to the recommendations made in conjuction with the approval, and to recommendations made pursuant to a Technical Systems Audit and an Audit of Data Quality conducted at Versar on January 15, 1987. The final revised QAPP was submitted February 3, 1987.

### Task 2: Limited Literature Review

A review of the published literature on the characterization of MWC residues was conducted. The scope of the review was limited to an extension of more comprehensive reviews conducted previously and in progress at the time of this study for the EPA Office of Solid Waste.

The review was intended to (1) ensure that this study did not merely duplicate the MWC characterization work of others, (2) provide data for comparison with results of analyses obtained in this study, and (3) cover portions of the published literature which other studies may not have adequately examined.

Task 3: MWC Residue Sampling and Analysis

This task was conducted in six (6) Subtasks as described below. EPA/HWERL assisted in identifying and assuring access to the MWC facilities at which samples were collected.

Subtask 1 -- Preliminary Survey of Facilities

The lead technicians for each of two sampling teams with the supervision of the Project Manager and the Task Manager, made telephone contact with personnel at MWC facilities identified in order to (1) acquaint facility personnel with the objectives of the study, (2) determine general operating characteristics of the facilities (type of combustor, characteristics of wastes accepted, combustor operating conditions, etc.), (3) determine locations for sampling solid residues, field leachate and ground water, and (4) schedule dates for preliminary site inspection and sampling. These telephone interviews also established whether the facility met the selection criteria as discussed in Section 3 of this report.

Subtask 2 -- Initial Site Visit and Inspection

The lead technicians for each sampling team and the Task Manager visited each of the four MWC facilities identified to obtain additional detail on facility operation, locate points of access for collecting residue samples, identify locations for sampling field leachate and ground water (if any), and establish working relationships with facility personnel.

### Subtask 3 -- Sample Collection

Samples of MWC solid residue, field leachate, and ground water were collected at sampling points identified in Subtask 2 above.

The lead technician and one addition sampling technician collected the samples. Procedures for sample collection, preservation, documentation, and shipment to the laboratory are described in detail in Section 3 of this report.

The number of samples of each medium actually collected are summarized in Table 1.1 below.

TABLE 1.1 SAMPLES COLLECTED FROM MWC FACILITIES(1)

| | Liquid Samples | | | Solid Samples | | |
|---|---|---|---|---|---|---|
| Facility | Field Leachate | Ground Water | Quench Water | Bottom Ash(2) | Fly Ash(2) | Landfill Composite |
| A | 0 | 1 | 2 | 6 | 7 | |
| B | 3 | 1 | 3 | 6 | 6 | |
| C | 3 | 4 | 2 | 7 | 9(3) | 1 |
| D | 3 | 0 | 3 | 6 | 7 | 1 |

---

(1) Samples include the following duplicates

| | | | | | | |
|---|---|---|---|---|---|---|
| A | --- | --- | --- | 1 | 2 | --- |
| B | --- | --- | 1 | 1 | 1 | --- |
| C | --- | --- | --- | 2 | 1 | --- |
| D | 1 | --- | 1 | 1 | 2 | --- |

(2) Samples include one composite at each facility for preparation of laboratory leachates, plus 3 composite duplicates.

(3) Samples include grab samples of 3 different size fractions of fly ash.

In addition, 4 trip blanks consisting of deionized water from the Versar laboratory, carried to the facility, handled like a sample, and returned for analysis were taken. And 2 field blanks consisting of deionized water poured over and through the cleaned sampling devices and returned for analysis were collected.

### Subtask 4 -- Sample Analyses

Solid residue samples (fly ash and bottom ash) and liquid samples (field leachate, ground water and quench water) and leachates prepared in the laboratory from the solid residue samples were analyzed for various heavy metals and organic compounds. The laboratory leachates were prepared using the Extraction Procedure (EP), the Toxicity Characteristic Leaching Procedure (TCLP), and the Mono-fill Waste Extraction Procedure (as described in SW-924). Sequential extractions were performed using the monofill waste extraction procedure. Total Organic Carbon (TOC) analyses were performed on all field water samples (plus blanks) and on the laboratory leachates prepared by the SW-924. Analyses for total metals were performed on all field water samples, laboratory leachates, and solid residue samples.

An organic scan was performed on field water samples and laboratory leachates to determine whether organic compounds other than PCDDs, PCDFs, and PCBs were present. Selected field water samples and laboratory leachates were solvent extracted and the compounds present in each fraction (acid and base/neutral) were identified and quantified by GC/MS techniques (EPA Method 625). The selection of the field water samples and laboratory leachates for extraction and GC/MS analysis was based largely on the TOC concentrations.

Analyses for PCDDs and PCDFs were performed by the Battelle, Columbus laboratory (Versar's subcontractor for these analyses) on all fly ash samples and on selected bottom ash and field water samples. In addition, analyses were performed on TCLP leachates of 8 ash samples. PCDD/PCDFs were identified and quantified at the homolog level; the 2,3,7,8 tetrachlorodibenzo-dioxin isomer was quantified separately.

Analyses for PCBs were performed on all solid residue and field water samples. No PCB analyses were performed on laboratory leachates. The PCBs were identified and quantified at the homolog level rather than as Arochlors.

The numbers of analyses for each group of constituents in each medium actually performed in this study are summarized in Table 1.2.

TABLE 1.2 NUMBERS OF ANALYSES PERFORMED
(Including duplicates, trip blanks and field blanks)

| Analyses | Field Liquid Samples | Laboratory Leachates | Solid Residues |
|---|---|---|---|
| TOC | 31 | 20(1) | |
| Metals(2) | 29(3) | 48 | 42 |
| Organic Scan(4) | 24(5) | 44 | |
| Organic Constituents | | 32 | |
| PCB | 27 | | 45 |
| PCDD/PCDF(6) | 22 | 8(7) | 43 |

(1) Total organic carbon (TOC) analyses not performed on laboratory leachates prepared by the EP and TCLP procedures because acetic acid is used for pH adjustment.

(2) Total metals include copper, chromium, cadmium, lead, arsenic, selenium, mercury, iron, manganese, zinc, and nickel.

(3) Duplicates and field blanks, but not trip blanks.

(4) The organic scan consists of extraction with Freon 113 and quantification of total organics using an infrared spectrophotometer.

(5) No duplicates performed on the organic scan.

(6) Analyses performed by subcontractor (Battelle Columbus Laboratories).

(7) PCDD/PCDF analyses of TCLP leachates, one from each solid residue composite from each facility.

### Subtask 5 -- Analytical Data Management

The analytical data from the laboratory were entered into a computer system (i.e., IBM-PC and Lotus 1-2-3 software) to generate data tables and graphs. Field data, that is information describing the MWC facility design and operating conditions, were also entered into the data base. The data were arranged by MWC facility and variable or chemical constituent. In cases where data comparisons would be meaningful (e.g., to examine the differences between laboratory leachate and field water sample analyses), the data were grouped together or graphs were prepared thereby highlighting significant trends. The compilation of all analytical data includes the presentation of all quality assurance/ quality control data (e.g., results form the analysis of replicates, percent recoveries of spikes or surrogates).

### Subtask 6 -- Ongoing QA Review

The analytical and quality assurance/quality control procedures were detailed in the QAPP for this project. Each of the analytical procedures (e.g., typically CLP methods) employed include quality control measures to evaluate the performance of the method on a continuing basis. These performance criteria were evaluated as specified by the method by the laboratory and project QA/QC officer, and any deficiencies were resolved either through re-analysis of the sample or the application of appropriate correction factors. In addition, replicate analyses were performed on 25 percent of all samples tested. The results of the replicate analyses, as well as the procedural performance checks (e.g., spike or surrogate recoveries), are presented in a separate section of this report so that the information may be interpreted in terms of the actual level of confidence of the data.

### Task 4: Data Evaluation

As the analytical and quality control data became available, efforts were directed toward reviewing the data and field notes and interpreting the results. Based on EPA's concern regarding the environmentally safe disposal of MWC residues, the following technical concerns were addressed during the evaluation of the data:

1. Recent data available in the literature suggests that toxic constituents (e.g., metals, organics) may be present in solid waste residues generated by MWC facilities. The data derived from this study were used to further examine whether a problem associated with the land disposal of MWC residues exists.

2. The results of the analyses of the field water samples and laboratory leachates were compared to determine if any of the laboratory leaching procedures accurately model the constituents found in the field water samples.

3. At each MWC facility, operating data were collected to characterize the combustion conditions which resulted in production of the residues that were sampled. The results of the chemical analyses of solid and liquid samples, and laboratory leachates were examined with respect to the combustion conditions to identify any significant correlations.

### Task 5: Project Report and Summary Report Preparation

The project report (including draft and final) has been prepared by the Versar technical specialists who were assigned as team leaders for each facility sampled. Versar senior scientists contributed to and reviewed the report to ensure that the overall project objectives are met and that the final report is technically sound and complete.

The report includes:

- Results of the literature review.
- All analytical results and field observations.
- All quality assurance and quality control and data.
- An interpretation of the significance of the data in light of current disposal practices for MWC wastes and the findings of other groups working on MWC residues.

A Project Summary will be prepared, based on the draft report, to be published by EPA and included in the EPA/600 series of Research and Development Project Summaries.

## 2.0 REVIEW OF PERTINENT LITERATURE

Versar performed a limited literature review to obtain pertinent information from previous studies of municipal waste combustion (MWC). This review focused on acquiring literature that contained MWC residue characterization data. This acquired data was then used for a comparative evaluation with the MWC residue characterization data generated in this study (see Section 5.1).

The literature review was performed by using the following sources: a database of abstracts on MWC ash literature compiled by the University of Massachusetts; the Dialog computer user service, which is a compilation of technical document abstracts that are accessed by "keywords" (e.g., fly ash, bottom ash, municipal waste combustion, leachate, etc.); and Versar's in-house technical documents. These sources were used to obtain more than 250 abstracts from potentially pertinent documents. Then, each of the abstracts was read to determine whether the publication contained information warranting its acquisition. Because the focus of the literature review was MWC residue characterization data, the publications describing topics such as incinerator design, landfill design, analytical techniques for characterizing the residue, stock sampling and analysis, and residue utilization were omitted from any further consideration.

After the review of the abstracts was completed, 78 documents were identified as potential sources of MWC residue characterization data were acquired. The identified documents are listed in Appendix A. Each of these documents was scanned to extract data for metals, polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins/polychlorinated dibenzofurans (PCDD/PCDF), and organic constituents (i.e., base/neutral and acid extractable semi-volatile compounds-BNAs) in solid samples (e.g., fly ash and bottom ash), laboratory leachates prepared from these solid samples, and field water samples (e.g., field leachate, quench water, and ground water). This scan of the publications revealed an abundance of data for metals and PCDD/PCDF in solid samples, indicating that the metal and PCDD/PCDF composition of the solid MWC residues has been extensively studied. This information was extracted from the publications and is summarized in Section 5.1 (see Tables 5.1 and 5.3). A limited amount of data was also available for PCBs in solid samples; metals in Extraction Procedure (EP), Toxicity Characteristic Leaching Procedure (TCLP), and deionized water laboratory-prepared leachates; and metals and BNAs in field water samples, including quench water and field leachate. This information is also summarized in Section 5.1 (see Tables 5.2, 5.4, 5.5, 5.6, 5.7, and 5.8). Finally, the reviewed publications did not contain any data for PCDD/PCDFs and BNAs in laboratory-prepared leachates, or for PCBs and PCDD/PCDFs in field water samples, indicating that the previous studies did not address these contaminant/matrix combinations.

## 3.0 APPROACH TO STUDY

This section discusses in detail the approach employed in this investigation. Section 3.1 describes the process of selecting the four MWC facilities sampled including the selection criteria and the identification and selection process. Section 3.2 provides a description of each of the facilities selected including the design and operating characteristics of the combustor units and pertinent characteristics of the landfills into which the MWC residues are disposed. Section 3.3 details the sampling procedures, sampling locations and samples collected at each facility. Section 3.4 describes the procedures used in the laboratory for preparing leachates, and the procedures for analyses of all samples and laboratory-prepared leachates.

### 3.1 Municipal Waste Combustor Facility Selection

Four MWC facilities were selected for residue chemical characterization. These facilities were chosen to (1) represent MWC facilities generally in design and operating features, (2) provide a range of design and operating features such that any difference observed in the chemical characteristics of the residues could possibly be qualitatively related to design and operating features, and (3) provide samples of landfill leachate generated exclusively from MWC residues rather than from mixtures of MWC residues and other solid wastes.

#### 3.1.1 Facility Selection Criteria

The four MWC facilities studies in this project were selected from a larger group of facilities known to EPA/HWERL and EPA/OSW in accordance with the following criteria:

1. Facility Types - Two facilities were to have resource (e.g., energy or material) recovery processes, and two were to be operated solely for waste volume reduction.
2. Information Availability - Each facility was to be currently active and was to have information available on the engineering design, operating characteristics (e.g., times, temperatures, refuse feedrate, etc.), raw waste characterization (e.g.,

amounts of industrial wastes accepted and approximate percentages of paper, food, plastic, textiles, etc.), and relative amounts and disposition of the various MWC residues (e.g., fly ash, bottom ash, quench water, etc.).

3. Landfilling of Solid Residues - Each facility was to have disposed of the MWC residues in a cell or landfill separate from other solid or hazardous wastes.

4. Suitability of Sampling Locations - The MWC facility and the landfill should be designed to permit the collection of discrete samples of the individual residues (fly ash, bottom ash, quench water).

5. State and Facility Cooperation - To ensure that the sampling and information gathering efforts would be performed in an efficient and timely manner without obstructions due to any policy or regulatory enforcement issues, representatives of the cognizant state regulatory agency and of the facility should be willing to cooperate with EPA/HWERL and contractor personnel.

Criteria 2, 3, and 5 were considered absolute, i.e., no facility would be selected that did not meet these three criteria. With respect to Criterion 1, it was important that both resource recovery and volume reduction facilities be studied, but the relative proportions of the two types were flexible. In fact, among the four MWC facilities selected, three were energy recovery facilities (one with a material recovery process proceeding combustion) and one was a volume reduction facility. With respect to Criterion 4, optimally separate samples of fly ash and bottom ash should be collected. However, combined bottom and fly ash samples were considered acceptable if a separate fly ash sample could be collected and the approximate fraction of fly ash in the combined ash was known.

Other desirable features of the MWC facilities included the following:

- The landfill containing the mono-filled MWC residues should have an operating leachate collection system from which samples of field leachate could be collected. Alternatively, locations, where leachate could be obtained should be available.

- Monitoring wells from which ground water samples could be collected should be located down gradient in a water-bearing zone potentially affected by leachate from the landfill.

### 3.1.2 Identification and Selection Process

EPA/HWERL and EPA/OSW first identified the states which currently require that MWC residues be disposed of in a separate cell or landfill. This assured that any facility selected would have a monofill disposal area rather than a landfill with co-disposed solid wastes and/or hazardous wastes. EPA/HWERL subsequently contacted representatives of the cognizant regulatory agencies within each state to (1) enlist their cooperation in the project, and (2) determine MWC facilities that might meet the selection criteria. Subsequently, letters were sent to the state regulatory agencies describing the objectives of the project, presenting a timetable for facility selection and sample collection, and formally requesting the state agency's assistance.

The state agencies agreeing to assist the project then contacted the facilities to briefly describe the project and to enlist the cooperation of facility representative. Upon receipt of notification that facilities had been contacted and had agreed to cooperate in the project, letters were sent from EPA/HWERL to the individual facilities describing the objectives of the project, and proposing a schedule for initial telephone interviews, site visits, and sample collection by Versar personnel.

Once agreement had been reached of the facility's cooperation in the project, Versar personnel contacted facility representatives by telephone and obtained specific detailed information on the combustor facility design and operating characteristics including the feed waste materials, ash handling system, residue disposal practices, characteristics of the disposal cell or landfill, and the availability of locations for sample collection. A questionnaire was developed and used for guidance in conducting these telephone interviews.

The information obtained in the telephone interviews was used to make the final selection of the four facilities to be sampled. Some facilities initially considered were eliminated at this point.

Subsequently, the Versar lead sampling technician and the Task Manager (or designee) visited the facility to determine exact sampling locations and the working conditions to be encountered during sampling, and to make final arrangements with facility personnel on sampling schedule and any special assistance required during sampling. The information obtained in these initial site visits was used to plan the sampling activities, including the sampling equipment and sample containers required, and the sampling strategy (e.g. time compositing versus spatial compositing). The actual sampling was conducted within three weeks of completion of the initial facility visits. Sampling locations and procedures are described in detail for each facility in Section 3.3.

### 3.1.3 Conformance to Selection Criteria

The degree to which each facility selected met the criteria for selection is summarized in Table 3.1.

Among the four facilities, three were operated for energy recovery with one (Facility A) having some limited capability for recovery of aluminum from the feed prior to combustion. One facility was operated for volume reduction only.

All four facilities provided detailed information on the combustor design and operating characteristics and made available as much information as they had on the design of the landfill receiving the solid residues. At all four facilities, the solid residues were disposed in monofill landfills.

At three of the facilities, bottom ash and fly ash were combined and there was no feasible way to collect a separate bottom ash sample. At all facilities, however, separate fly ash samples were collected.

TABLE 3.1 FACILITY CONFORMANCE TO SELECTION CRITERIA

| CRITERIA | FACILITY | | | |
|---|---|---|---|---|
| | A | B | C | D |
| 1. Facility Types | RR/ER | ER | VR | ER |
| 2. Information Available | Yes | Yes | Yes | Yes |
| 3. Monofill Disposal | Yes | Yes | Yes | Yes |
| 4. Sampling Locations | Fly & Combined | Fly & Bottom | Fly & Combined | Fly & Combined |
| 5. State/Facility Cooperation | Yes | Yes | Yes | Yes |
| Other: | | | | |
| • Leachate Collection System | No | No | No | No |
| • Monitoring Wells | 1 | 1 | 4 | 0 |

RR = Resource Recovery; aluminum recovery before combustion.
ER = Energy Recovery as steam.
VR = Volume Reduction only.

Although some of the landfills associated with the facilities had leachate collection systems in place, none were functioning as designed at the time of sample collection for this study. Samples of field leachate were collected at three of the facility landfills (B, C, and D) at locations of opportunity as described later.

Suitably-placed monitoring wells were available and were sampled at three of the facilities (A, B, and C).

Overall, the criteria for facility selection were achieved with reasonable success in the four facilities selected. The two main areas of deficiency with respect to the criteria were in the access to fly ash and bottom ash separately in the ash processing line and the lack of functioning leachate collection systems at landfills.

Further inquiry by Versar personnel has indicated that few combustor designs provide access to fly ash and bottom ash separately. In the limited time available to conduct the search for MWC facilities, it was not possible to locate more than one such combustor.

A leachate collection system, which was present at only one facility had apparently become clogged and was not draining. This may be a pervasive problem with mono-filled disposal cells containing MWC residues which have been in operation for more than a few years.

## 3.2 Facilities Selected

Based upon the selection criteria presented in Section 3.1.1 and the involvement of EPA and appropriate state agencies, four facilities were selected for MWC residue characterization sampling. Because each of the facilities was assured that the source of the data for this study would not be identified, the facilities were generically designated throughout this report as Facility A, B, C, and D. After the facilities were selected, they were contacted by telephone and visited prior to sampling, to obtain operating and design characteristics of the incinerators and their associated landfills. Sections 3.2.1 through 3.2.5 present descriptions and summary tables of these operating and design characteristics for each facility.

### 3.2.1 Facility A

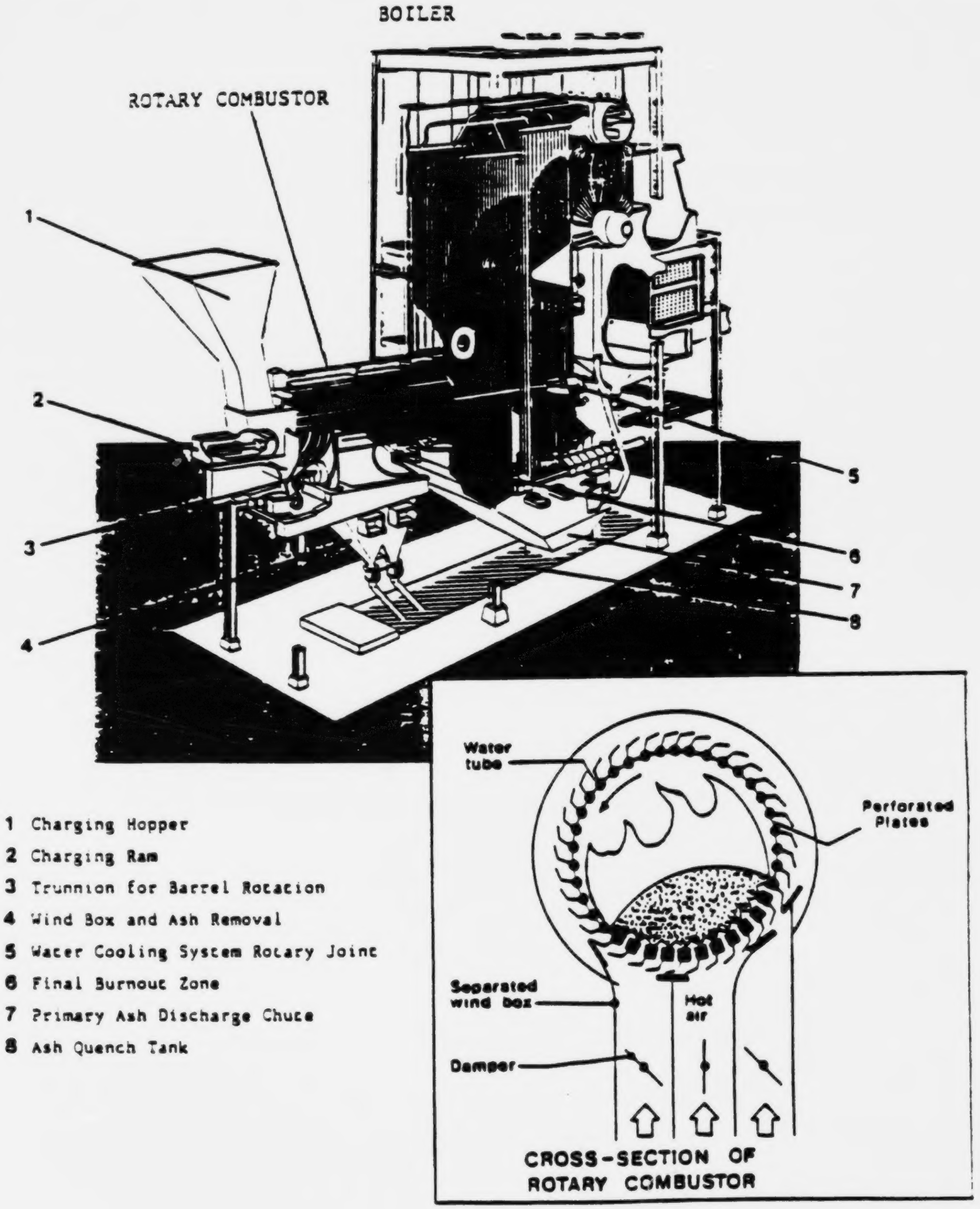
Facility A operates two water-wall rotary combustors which were put on line in December 1981 and March 1982. Figure 3.1 presents a diagram of a typical rotary combustor. The units are each rated at 100 tons per day and operate 24 hours per day, 7 days per week. The total actual operating capacity is about 150 to 180 tons per day, depending on the moisture content of the feed. Each unit is equipped with a mechanical cyclone separator and an electrostatic precipitator.

The units were originally the same, but Unit 2 has been retrofitted to provide better air control. The majority of the air to Unit 1 is overfire. Unit 2 was retrofitted to better control the percentage of overfire and underfire air.

The units are monitored using televisions to maintain the fire in the middle of the combustor area. In addition, oxygen, carbon monoxide, furnace temperature, and residues are monitored to determine the combustion efficiency. The feed rate and the amount of combustion air are changed to control the combustion.

The feed to the units is approximately 50 percent residential and 50 percent industrial (i.e., construction type refuse including wood, plastic, and metal). The facility has the ability to separate glass, iron, and aluminum from the feed, but does not process all feed to the combustors. From the refuse pit, the bucket feeds the two charging hoppers (See Figure 3.1) to the combustors and the charging hopper to the separation process. The processed feed is discharged back into the refuse pit, where it is used to feed the combustor charging hoppers. Occasionally, the refuse in the pit covers the inlet or the outlet of the separation process making it impossible to process refuse. When refuse

Figure 3.1 Facility A Combustor


BOILER
ROTARY COMBUSTOR
1
2
3
4
5
6
7
8
Water tube
Perforated Plates
Separated wind box
Hot air
Damper
CROSS-SECTION OF ROTARY COMBUSTOR

1 Charging Hopper
2 Charging Ram
3 Trunnion for Barrel Rotation
4 Wind Box and Ash Removal
5 Water Cooling System Rotary Joint
6 Final Burnout Zone
7 Primary Ash Discharge Chute
8 Ash Quench Tank

is processed, the aluminum is recycled, but the glass and iron are disposed at the landfill along with the ash.

The residues from the combustors include bottom ash, fly ash, and quench water. The units achieve approximately 90 percent reduction by volume and 50 to 60 percent reduction by weight of the incoming refuse. The bottom ash falls into a quench tank and is drag conveyed to a temporary storage bin which has sufficient capacity to hold the ash produced over 4 hours (i.e., 14 to 18 cubic yards). The fly ash, which is removed from the flue gas using mechanical cyclone separators and electrostatic precipitators, enters a turbulator where water is added. The fly ash feeds to the quench tank displacing some quench water. The displaced quench water (i.e., approximately 10 to 15 gallons per minute total) overflows to a sump where solids are removed The effluent from the sump is discharged to the sanitary sewer. The bottom and fly ash, along with non-combustible and large items (i.e., large metal items, tires, wood palettes, furniture, etc.), are transported to a landfill a total of about 12 times per day.

The landfill is located about 13 miles northwest of the facility. It was used for municipal refuse until about early 1982 when the combustors came on line. The landfill is now used for ash, separated glass and iron, and large items. The ash has been segregated from the municipal refuse. A small creek runs close to the landfill (i.e., 200 yards). There is no leachate collection system, but there are two ground-water monitoring wells in the new section of the landfill where the ash is placed. The landfill is surrounded by a berm that limits the release of surface runoff to adjacent areas. One monitoring well that is closer to the older ash is reported to be frequently dry. The second monitoring well, which contains water, is closer to the freshly placed ash, but at quite a distance (i.e., 400 to 500 feet). The landfill is covered daily with soil.

### 3.2.2 Facility B

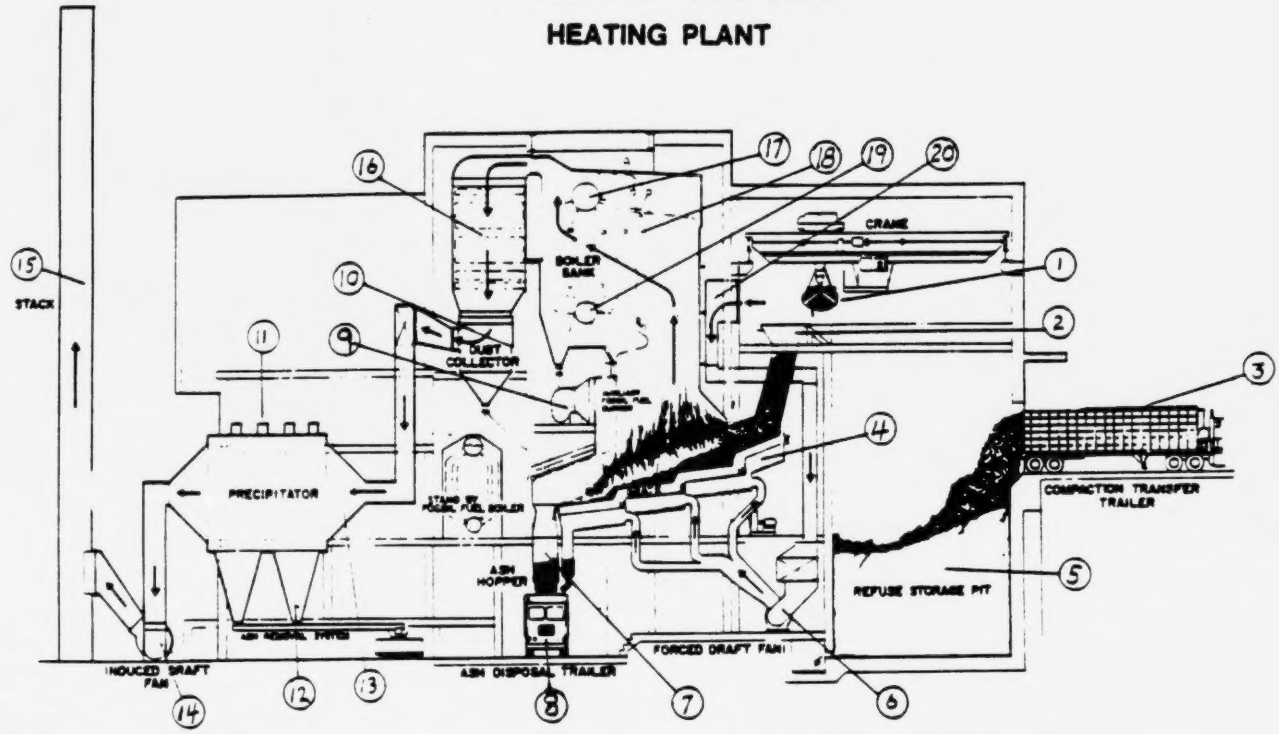
Facility B operates three water-wall traveling grate mass burn combustors similar to the unit shown in Figure 3.2. Units 2 and 3 were put on line in 1974. Unit 4 was put on line in September, 1986. Units 2 and 3 are each rated at 360 tons per day, and Unit 4 is rated at 400 tons per day. The units operate 24 hours per day, 7 days per week. The total actual operating capacity is about 600 to 700 tons per day, but will be up to 900 tons per day when Unit 4 is completely operational. The feed to the units is approximately 80 percent residential and 20 percent commercial. Combustion efficiency is controlled by changing the amount of underfire air to produce the required steam flow (i.e., 80,000 lbs/hour each unit). Each unit is equipped with a cyclone and an electrostatic precipitator for particulate control.

The residues include bottom ash, fly ash, and quench water. The units achieve approximately 90 percent reduction by volume and 70 percent reduction by weight of the incoming refuse. The bottom ash is spray quenched (i.e., approximately 20 to 25 gallons per minute each unit), stored in an enclosed hopper, and discharged into a disposal trailer (See Figure 3.2) about every two hours (i.e., 3 to 4 hoppers of bottom ash per combustor per shift). Each trailer has sufficient capacity to hold two bottom ash dumps. Fly ash from each unit is removed from the flue gas stream in separate cyclones and electrostatic precipitators, mechanically conveyed (i.e., screw conveyors) to a combined duct, and discharged to an enclosed storage bin through a large hose. The quench water is discharged from the bottom ash hoppers, spills to the pavement below, and is collected in a surface drain. The quench water is discharged to the sanitary sewer after solids are removed in a sump.

The landfill is located about five miles east of the facility and has been used for the disposal of bottom ash and fly ash for about 4 to 5 years. The landfill was estimated to be approximately 15 acres (rectangular) in surface area and about 40 feet deep. The ash is

Figure 3.2 Facility B Combustor

INCINERATOR SIDE VIEW
HEATING PLANT



STACK
CRANE
BOILER BANK
DUST COLLECTOR
PRECIPITATOR
STAND BY FOSSIL FUEL BOILER
ASH HOPPER
ASH REMOVAL SYSTEM
INDUCED DRAFT FAN
ASH DISPOSAL TRAILER
FORCED DRAFT FAN
REFUSE STORAGE PIT
COMPACTION TRANSFER TRAILER
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1. CRANE
2. CHARGING HOPPER
3. SOLID WASTE COMPACTOR TRAILER
4. FOUR LEVEL RECIPROCATING GRATES
5. SOLID WASTE STORAGE PIT
6. FORCED DRAFT FAN
7. ASH HOPPER
8. ASH DISPOSAL TRAILER
9. AUXILIARY BURNER
10. DUST COLLECTOR
11. PRECIPITATOR POWER SUPPLY
12. ASH REMOVAL SYSTEM
13. ELECTROSTATIC PRECIPITATOR
14. INDUCED DRAFT FAN
15. STACK
16. ECONOMIZER
17. TOP OR STEAM DRUM
18. SUPER HEATER
19. LOWER DRUM
20. FORCED AIR INLET

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disposed of in 10 foot layers and covered with soil. A river is in proximity to the landfill (i.e., approximately 100 yards). There is no leachate collection system, but there are four ground-water monitoring wells. Surface runoff is controlled with hay bales along the sides of the landfill. The two wells closest to the active area of the landfill are often dry. The two wells closest to the older portion of the landfill contain water, but one well is at a very steep angle.

### 3.2.3 Facility C

The incinerator at Facility C includes two units, each consisting of a reciprocating grate and a rotary kiln combustor. The incinerator was brought on line in January 1970, and currently a third unit is being added to the facility. The new unit will be equipped with a boiler and a generator for energy recovery, and it should be operational by late 1986 or early 1987. If the new unit is efficient and cost effective, then the existing units will be retrofitted with energy recovery systems in the future. The two existing units are mass burn, volume reduction units without resource recovery. Figure 3.3 presents a diagram of the incinerator.

The existing units are identical, each having a rated capacity of 300 tons per day. The actual operating capacity for each unit is approximately 250 tons per day. The units operate at approximately 1600°F to 1800°F, and no additional fuel is used for burning the refuse. The units have a residence time for combustion of 30 to 45 minutes. Each unit is equipped with a crude economizer to remove the coarse fly ash, a cooling chamber to remove the medium fly ash, and an electrostatic precipitator to remove the fine fly ash.

The units are monitored in the control room to ensure that optimum combustion efficiency is maintained. The excess air, reciprocating grate combustion chamber temperature, rotary kiln combustion temperature, carbon monoxide, feed rate, and residue generation are monitored. The feed rate and overfire air are continually adjusted to maintain efficient operation.

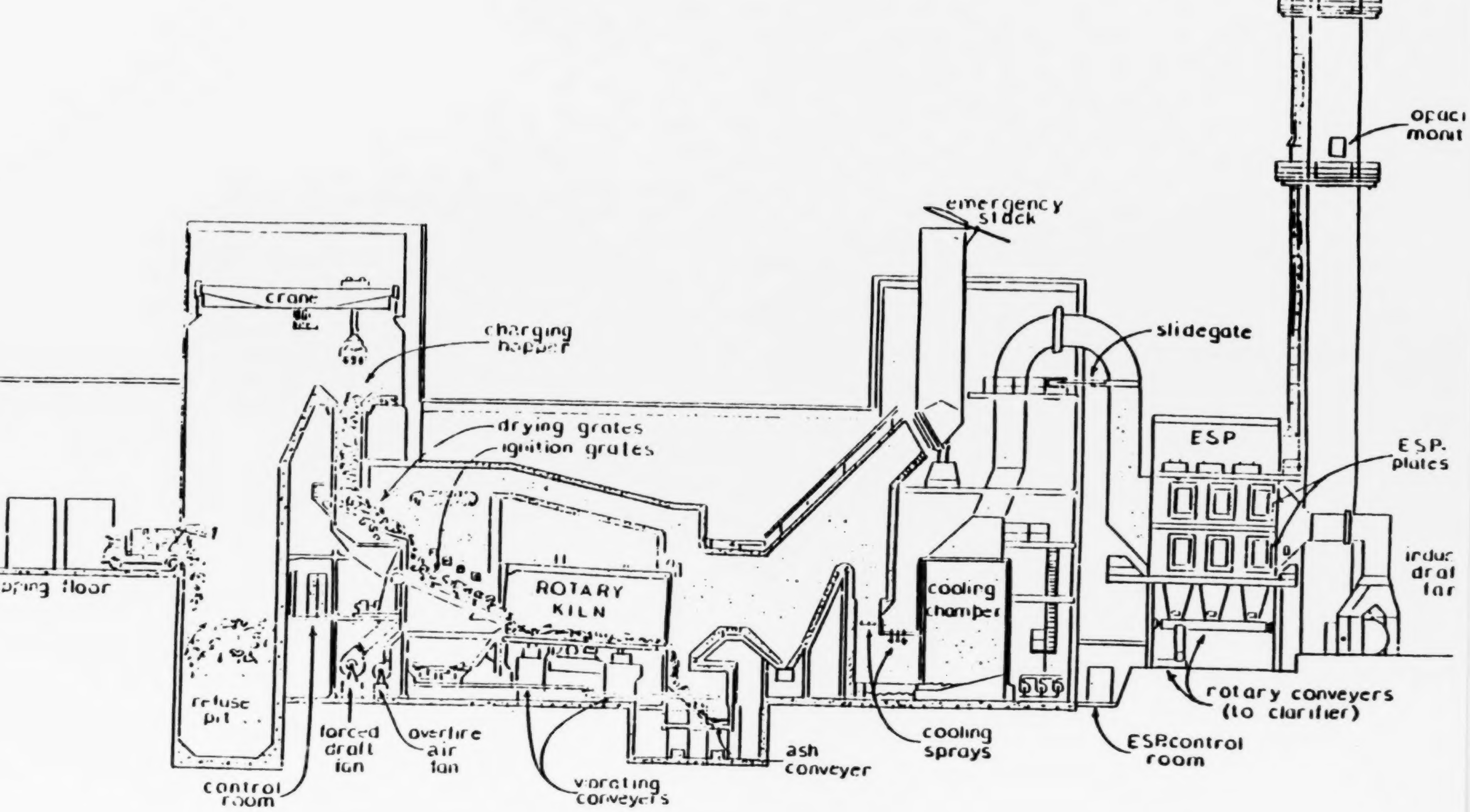

crane
charging hopper
drying grates
ignition grates
tipping floor
refuse pit
control room
forced draft fan
overfire air fan
ROTARY KILN
vibrating conveyers
ash conveyer
emergency stack
cooling chamber
cooling sprays
slidegate
ESP
ESP. plates
rotary conveyers (to clarifier)
ESP.control room
opaci
monit
induc
draf
fan

Figure 3.3 Facility C Combustor

The feed to the units is approximately 50 percent residential and 50 percent industrial (i.e., paper, wood, plastics, and metals). The facility does not process the waste before combustion, however, large objects (e.g., tires, refrigerators, stoves, water heaters, etc.) are removed by the feed crane operator, if noticed. The refuse is gravity fed into the incinerators; it has a heating value of approximately 5000 BTU's per pound. Each unit burns approximately 75,000 tons of raw trash per year.

The residues from the combustors include bottom ash, fly ash, and quench water. The units achieve a volume reduction of 90 percent and a weight reduction of 70 percent over the raw refuse. The bottom ash falls into a quench water tank and is transported to a temporary storage bin by a drag conveyor. The fly ash is transported by a screw conveyor and a trough to the quench water tank, where it is removed with the bottom ash. The displaced quench water overflows into a settling tank, where the solids are removed. The clarified quench water overflows a weir at the end of the settling tank into a wet well (i.e., sump), and then discharges to the local wastewater treatment plant. The bottom ash, fly ash, and materials removed prior to combustion are trucked to the on-site landfill for disposal.

The landfill is constructed as a series of hills and valleys, where the natural valleys are being filled with the combustion residues. The landfill has been used since 1970, and is expected to be used until the year 2050. There is no leachate collection system, however, there is a seep where field leachate may be collected. The landfill is situated very close to two streams. The one stream is fairly small, and the landfill actually extends over top of the stream with a culvert beneath it. The other stream is a major river approximately 300 yards away from the landfill. There are three monitoring wells and a production well located in between the landfill and river. On a daily basis, waste is disposed by dumping the loads of residue on top, and then pushing the fresh loads down the sides with a bulldozer.

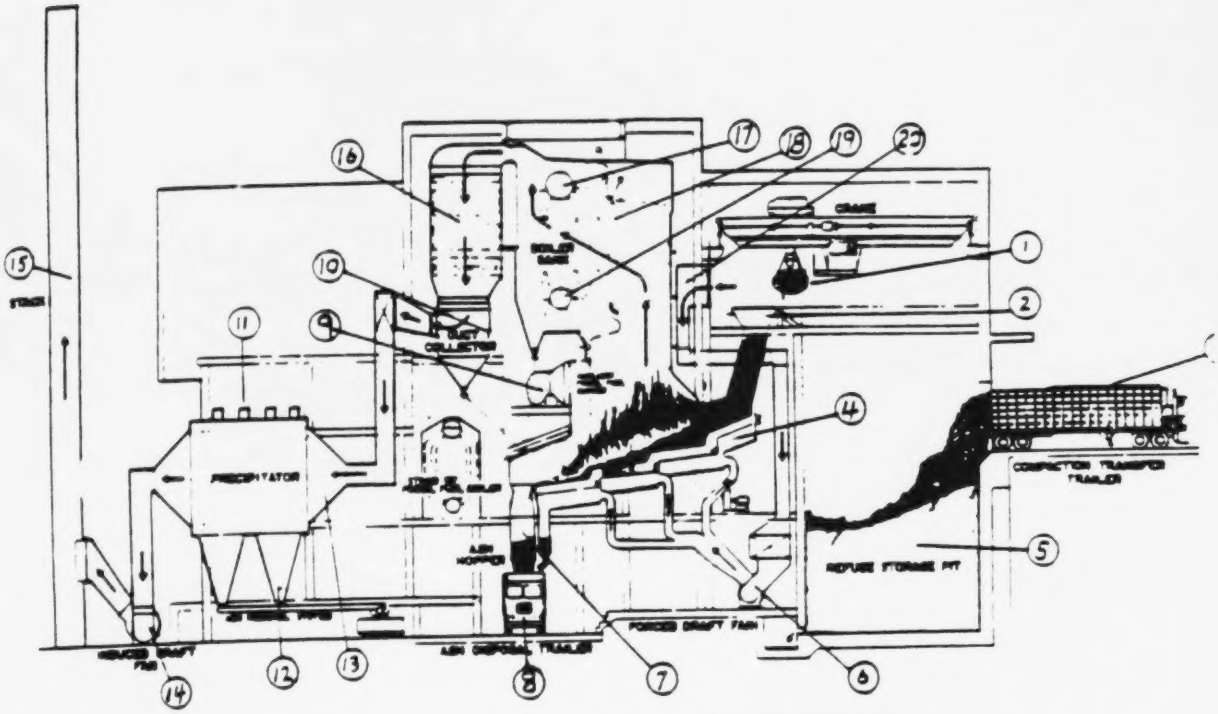
### 3.2.4 Facility D

The Facility D incinerator consists of two identical water-wall traveling grate mass burn combustors similar to the unit depicted in Figure 3.4. The facility's construction began in December 1969, and the facility began operating in October 1972. The units are rated at 360 tons per day each, however, the actual operating capacity is approximately 310 tons per day for each unit. However, if the refuse feed is less than 5000 Btu's per pound, the feed rate is slowed to allow for longer residence times and more complete combustion. The units operate 24 hours per day, 7 days per week, 50 weeks per year, with approximately 2 weeks per year for maintenance. The units typically operate at approximately 1500°F, and no additional fuel is used for the combustion. The residence times within the units range from 4 to 5 hours with the longer residence times necessary for wet feed refuse. The units are equipped with economizers and electrostatic precipitators for removing fly ash. Steam is generated by the progressive cooling of the furnace gases by the welded-membrane water-cooled walls of the combustion chamber, and by the five passes of the hot gases through the convection and generating sections of the boiler. Each boiler has a continuous steam generating capacity of 92,500 lbs/hr.

The units are monitored from a control room using television monitors and operating variables. The combustion temperature, oxygen, feed rate, and residue generation are all monitored. Presently, the combustion temperature is the major operational variable, however, the facility is switching to an oxygen monitoring system which was demonstrated to yield more efficient operation.

The feed to the units is approximately 50 percent residential and 50 percent industrial (e.g., wood, paper, plastics, metals, etc.). Additionally, in 1985 an automated sludge disposal system was added to permit the facility to incinerate sludge from the nearby wastewater treatment plant. The sludge is mixed with the refuse, and the feed rate

Figure 3.4 Facility D Combustor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STACK
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BOILER BANK
CRANE
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11
9
DUST COLLECTOR
4
PRECIPITATOR
COMPACTION TRANSFER TRAILER
ASH HOPPER
5
REFUSE STORAGE PIT
FORCED DRAFT FAN
ASH DISPOSAL TRAILER
INDUCED DRAFT FAN
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12
13
8
7
6

1. CRANE
2. CHARGING HOPPER
3. SOLID WASTE COMPACTOR TRAILER
4. FOUR LEVEL RECIPROCATING GRATES
5. SOLID WASTE STORAGE PIT
6. FORCED DRAFT FAN
7. ASH HOPPER
8. ASH DISPOSAL TRAILER
9. AUXILIARY BURNER
10. DUST COLLECTOR
11. PRECIPITATOR POWER SUPPLY
12. ASH REMOVAL SYSTEM
13. ELECTROSTATIC PRECIPITATOR
14. INDUCED DRAFT FAN
15. STACK
16. ECONOMIZER
17. TOP OR STEAM DRUM
18. SUPER HEATER
19. LOWER DRUM
20. FORCED AIR INLET

is controlled to maintain a combustion temperature of 1400°F to 1500°F. The facility does not process the waste prior to combustion, except that tires are removed and shredded before being burned. However, large noncombustible items (e.g., refrigerators, water heaters, etc.) are removed and sold for scrap metal.

The residues from the facility include bottom ash, fly ash, and quench water. The units achieve a volume reduction of 85 percent, not including the large materials removed before combustion. Bottom ash falls into a quench water tank and is transported by a conveyor belt to a temporary storage bin. Fly ash, which is removed by the economizer, drops down a chute into the quench water tank. The electrostatic precipitator ash is transported by a screw conveyor to the chute, where it joins the economizer ash and is subsequently gravity fed to the quench water tank. The quench water is removed with the ash, and the overflow is collected in a drain and routed to the wastewater treatment plant.

Trucks transport the bottom ash, fly ash, and associated quench water to the on-site landfill. The landfill is a tall mound located on a square area (approximately 500' x 500'). It has been in use for several years and is now overflowing. The landfill has a leachate collection system, however, the system is obstructed so leachate cannot be collected from this system. The facility does not have any ground water monitoring wells; it is only approximately one mile east of a major river.

### 3.2.5 Summary of Facility Design and Operating Characteristics

Several differences and similarities, which may contribute to the residue characteristics, were observed in the facility descriptions (see Sections 3.2.1. through 3.2.5) and are highlighted in this section. All four incinerators are less than 20 years old with capacities ranging from 200 tons per day (tpd) to 1120 tpd. One of the incinerators is relatively small (Facility A-200 tpd), while the other three are of medium size (600-1120 tpd). Two of the incinerators are traveling or reciprocating grate designs (Facilities B and D); the third is a rotary kiln design (Facility A); and the fourth is a combination of these two designs (i.e., reciprocating grate and rotary kiln in series for Facility C). Large metal objects (e.g., water heaters, refrigerators, etc.) and tires are removed at each incinerator prior to combustion, while only one incinerator (Facility A) processes its waste to remove iron, aluminum, and glass. All four incinerators are equipped with electrostatic precipitators to remove flue gas particulates, and two of the incinerators (Facilities A and B) are also equipped with cyclones to remove additional fly ash particles. A summary of the design and operating characteristics is presented in Table 3.2

The landfill for each facility is more than five years old and is a monofill with only combustion residues and non-combustibles, including tires, disposed. Three of the landfills (Facilities B, C, and D) are not adequately lined or capped, and therefore, they would be expected to produce and release leachates. This is potentially a problem because the landfills are generally close to the water table ($\leq$30 feet) and are in proximity to surface water. The fourth landfill (Facility A) is lined and capped with clay, and therefore, does not pose a significant leachate problem. Three of the landfills are near capacity and are expected to close by early 1987 (Facilities A, B, and D), while the fourth landfill is expected to be used for at least 60 more years. Table 3.3 presents a summary of the landfill characteristics.

### 3.3 Samples and Sampling Procedures

In order to meet the objectives of this study, Versar's personnel collected MWC residue samples and field water samples from the four facilities described in Section 3.2. These samples were collected between September 26 and October 22, 1986, and although the sampling locations and techniques were facility specific, the samples from each facility typically included: bottom or combined ash, fly ash, quench water, ground water, and field leachate. Additionally, composite samples of the fly and bottom ashes were collected for laboratory extraction

TABLE 3.2 MUNICIPAL WASTE COMBUSTOR DESIGN AND OPERATING CHARACTERISTICS

| Characteristic | Facility A | Facility B | Facility C | Facility D |
|---|---|---|---|---|
| Number of Combustors | 2 | 3 | 2 | 2 |
| Designation of Each Combustor | #1/#2 | #2/#3/#4 | #1/#2 | #1/#2 |
| Year of Construction | 1981/1982 | 1974/1974/1986 | 1970/1970 | 1972/1972 |
| Energy Recovery System | Yes | Yes | No | Yes |
| Type of Combustor | Continuous Feed Water-wall Rotary Kiln | Continuous Feed Water-wall Traveling Grate | Continuous Feed Reciprocating Grate Rotary Kiln | Continuous Feed Water-wall Reciprocating Grate |
| Capacity (tons/day) | | | | |
| o Design | 100/100 | 360/360/400 | 300/300 | 360/360 |
| o Operating | 75-90/75-90 | 275/275/300 | 250/250 | 310/310 |
| Operating Schedule Hours/day (days/week) | 24 (7) | 24 (7) | 24 (7) | 24 (7) |
| Design Combustion Temperature (F) | 1200 | 1800 | 1800 | 1400-1500 |
| Residence Time (hours) | 0.75 | 0.75 | 0.5 - 0.75 | 4 - 5 |
| Air Pollution Control System | Cyclone, ESP | Cyclone, ESP | ESP | ESP |
| Bottom Ash Handling System | Wet (Quench Tank) | Wet (Quench Tank) | Wet (Quench Tank) | Wet (Quench Tank) |
| Fly Ash Handling System | Wet (Quench Tank) | Dry | Wet (Quench Tank) | Wet (Quench Tank) |
| Quench Water Flow (gal/day) | 17,000 | 35,000 | 23,000 | 23,000 |
| Quench Water Disposal | POTW | POTW | POTW | POTW |
| Waste Composition (%) | | | | |
| o Residential | 50 | 80 | 50 | 50 |
| o Commercial/Industrial | 50 | 20 | 50 | 50 |
| Waste Processing or Pre-handling | Remove large objects; separate glass, iron, and aluminum for recyle | Remove large appliances and tires | Large items removed by crane operator | Remove tires and large noncombustible materials; recycle ferrous metals as scrap; periodically shred and burn tires |
| Refuse Storage Location and Capacity | Piled in pit; two-day capacity | Piled in pit; two-day capacity | Piled in pit; two-day capacity | Piled in pit; two-day capacity |

TABLE 3.3 LANDFILL CHARACTERISTICS

| Characteristic | Facility A | Facility B | Facility C | Facility D |
|---|---|---|---|---|
| Amount of Combustor Residue Disposed (tons/day) | 60 | 130 | 155 | 90 |
| Other Types of Waste Disposed | Tires, large items, construction debris and, nocombustibles | Large items and construction debris | Noncombustible items | Tires and noncombustibles |
| Year Landfill Began Operation | 1982 | 1981 | 1970 | Post 1980 |
| Projected Year Landfill Reaches Capacity | 1987 | 1987 | 2050 | 1987 |
| Shape | Rectangular | Rectangular | Rectangular (multiple mounds on hilly terrain) | Square |
| Lateral Dimensions (feet) | 500 x 1,000 | 500 x 1,000 | 300 x 1,500 | 500 x 500 |
| Depth Below Grade (feet) | <10 | 20 | 0 | 20 |
| Maximum Height Above Grade (feet) | 35 - 40 | 20 | 60 | 50 |
| Slope | Relatively flat with sloping sides | Relatively flat with sloping sides | Hilly terrain with numerous waste mounds | Single mound of waste with steeply sloped sides |
| Portion of Landfill That is Capped (%) | 90 | 90 | 0 | 0 |
| Cap Material and Thickness | Clay 3 feet | Native soil 6 - 12 inches | NA | NA |
| Leachate Collection System | None | None | None | Gravel (not functioning) |
| Runoff Control Measures | Impermeable cap; graded contour; diversion ditch around landfill perimeter | Relatively thin cap; hay bales around one corner of landfill to inhibit runoff | Adjacent mounds of waste tend to trap surface water; erosion of slope evident | Flat area adjacent to waste pile tended to collect surface water |
| Depth to Ground Water (feet) | 15 | 10 - 15 | 30 | >100 |
| Number of Monitoring Wells | 2 (one useable) | 4 (two useable) | 3 | 0 |
| Distance to Nearest Domestic Well | > 1/4 mile | < 500 feet | 1,000 - 1,500 feet | > 1/4 mile |
| Distance to Nearest Surface Water | 200 feet (small stream) | 200 feet (major river) | 1,000 feet (major river) | 1 mile (major river) |

using three different leaching procedures (i.e., Extraction Procedure, Toxicity Characteristic Leaching Procedure, and Mono-filled Waste Extraction Procedure). Where available, samples of disposed ash and discrete fly ash fractions were also collected to more adequately characterize the MWC residues and the environmental effects of their disposal. The following sections (See Sections 3.3.1 through 3.3.4) will describe, in detail, the samples, sampling locations, and sampling procedures for each of the four facilities.

### 3.3.1 Facility A

Versar personnel collected groundwater samples at Facility A's landfill on September 25, 1986 and MWC residue samples at Facility A on September 26, 1986. The MWC residue samples included: bottom/fly ash (i.e., a mixture of bottom ash and fly ash), fly ash, and quench water. As per sampling plan specifications, 25 percent of the samples were collected in duplicate for quality control (QC).

The MWC residue sampling at Facility A commenced at the beginning of the second shift (i.e., 7:00 a.m. to 3:00 p.m.) on Friday, September 26, 1986, and was completed at the end of the third shift (i.e., 3:00 p.m. to 11:00 p.m.) on Friday, September 26, 1986.

Units 1 and 2 were sampled separately to determine if any differences exist in the characteristics of the residues due to the independent operating parameters for each system.

Although the landfill at Facility A did not have a leachate collection system, the Versar monitoring team explored the perimeter of the landfill to find a natural seep for leachate collection. Such a location did not exist, so no field leachate samples were collected. However, at the request of EPA/HWERL, a follow-up visit was scheduled for October 22, 1986, to again attempt to collect a field leachate sample. Although the follow-up visit was scheduled after a period of heavy rain, the landfill perimeter was still dry with no natural seeps. Therefore, no field leachate samples could be obtained at Facility A.

While the samples were being collected, the combustor operator recorded pertinent operating data to be used for evaluating contaminant concentration differences between units, shifts, and facilities (See Section 5.0). This operating data is shown in Section 4.1, Table 4.1. Table 3.4 presents a summary, including field sample numbers, of the samples collected at this facility. Detailed descriptions of the sampling locations and procedures for each of the sample matricies are presented below.

Groundwater - The groundwater samples were grab samples collected the afternoon of September 25, 1986. There are two groundwater monitoring wells in the section of the landfill near where the ash is placed. One monitoring well that is closer to the older ash was dry. The second monitoring well which is closer to the freshly placed ash, is on a hillside approximately 400 to 500 feet from the active part of the landfill and contained water.

Prior to sampling the groundwater in the second monitoring well, the volume of standing water in the well casing and saturated annulus was determined by measuring and recording the well casing diameter, the depth from the top of the well casing to the water surface, and the depth from the top of the well casing to the sediment/water interface. The volume of standing water was approximately 0.8 gallons.

Because of the small volume of water and the reported slow recharging rate, the monitoring well was not evacuated. Instead, grab samples were collected from the standing water using a Teflon bailer. The water was clear with no visible particulate matter; therefore, the samples were not filtered. The clean, labeled sample containers (i.e., 4-oz. glass for TOC, 1-L glass for organic scan, 1-L plastic for metals, and one and a half 1-L glass for PCDD/PCDF) were filled directly from the Teflon bailer, documented on chain-of-custody forms, packed on ice in an Igloo-type cooler, and shipped to the laboratory by priority air express. The coolers were secured with EPA custody seals.

## TABLE 3.4 SAMPLE IDENTIFICATION CODES FOR FACILITY A

| Sample Matrix | Sample Description | TOC No. | Organic Scan No. | Metals No. | BNA No. | PCB No. | PCDD/ PCDF No. | Lab Leachate No. |
|---|---|---|---|---|---|---|---|---|
| Blank | Trip Blank | 17652 | 17653 | 17650 | 17654-57 | 17662-63 | 17658 | |
| Bottom/Fly | Composite | | | | | | | 17651 |
| Bottom/Fly | Unit 1, 9/26, AM | | | 17626 | | 17625 | 17624 | |
| Bottom/Fly | Unit 1, 9/26, PM | | | 17639 | | 17640 | 17641 | |
| Bottom/Fly | Unit 2, 9/26, AM | | | 17618 | | 17619 | 17620 | |
| Bottom/Fly | Unit 2, 9/26, AM, Dup | | | 17621 | | 17622 | 17623* | |
| Bottom/Fly | Unit 2, 9/26, PM | | | 17633 | | 17634 | 17635 | |
| Fly | Composite | | | | | | | 17648 |
| Fly | Composite, Dup | | | | | | | 17649 |
| Fly | Unit 1, 9/26, AM | | | 17627 | | 17628 | 17629 | |
| Fly | Unit 1, 9/26, AM, Dup | | | 17630 | | 17631 | 17632 | |
| Fly | Unit 1, 9/26, PM | | | 17636 | | 17637 | 17638 | |
| Fly | Unit 2, 9/26, AM | | | 17642 | | 17643 | 17644 | |
| Fly | Unit 2, 9/26, PM | | | 17645 | | 17646 | 17647 | |
| MWell | #1 | 18363 | 17506 | 18370 | | | 17523-24* | |
| Quench | Unit 1, 9/26 | 18362 | 17504 | 17501 | 17538-41 | 17546-47 | 17542-45 | |
| Quench | Unit 2, 9/26 | 18375 | 17505 | 18369 | 17548-51 | 17556-57 | 17552-55 | |

LEGEND:

Bottom/Fly = Combined bottom ash and fly ash samples
Fly = Fly ash
MWell = Groundwater from monitoring well
Quench = Incinerator quench water
TOC = Total organic carbon
BNA = Base/neutral acid extractable organics
* = Sample collected but not analyzed

Bottom/fly ash - The Versar monitoring team collected a combined ash (i.e., a mixture of bottom ash and fly ash) sample rather than a bottom ash sample because a location where a discrete bottom ash sample could be collected was not available. Each bottom/fly ash sample was a time-composite composed of eight grab samples representing each combustor/shift combination (i.e., Unit 1 or Unit 2, 2nd shift or 3rd shift).

During the 2nd shift, the grab sample portion of the time-composite sample was collected every hour over an eight-hour period. Unit 1 was having a clinker problem and Unit 2 was running raw refuse. The fourth grab sample from Unit 2 was collected after a 1-1/2 hour interval rather than a 1-hour interval because the drag conveyor had been shut off. The seventh grab sample from both units was collected after a 2-hour interval during which the Unit 2 conveyor had been shut off for about an hour. During the 3rd shift, sample increments were collected every 45 minutes over a five and one half-hour period. At the beginning of shift 3, Unit 1 was burning hot and the bottom ash on the conveyor was on fire; therefore, Unit 1 was not sampled for the first three grabs and the volume of the last five grabs was doubled. Unit 2 was still running cold. Per sampling plan requirements, the time-composite collected from Unit 2 during the second shift was split for field and laboratory control.

Each bottom/fly ash grab sample was collected from the quench tank drag conveyor of each unit. The drag conveyor transports the ash from the quench tank up an incline to a storage bin. As the ash is conveyer up the incline, the quench water returns down the slope to the quench tank. The bottom/fly ash is wet and contains uncombusted material (e.g., glass, cans, and metal scraps).

Each sample increment of the time-composite sample was collected by stopping the drag conveyor and by taking a stopped-belt cut (ASTM Method D2234-76) across the conveyor using a steel shovel. The cut was perpendicular to the conveyor direction and was the width of the shovel. The sides of the cut were as nearly parallel as possible to prevent particle-size bias. The incremental sample was placed in a polyethylene lined three-gallon collection bucket and was thoroughly mixed with a steel hand trowel. A 550-milliliter subsample (1,100 milliliters for the sample to be split) was transferred to a lined compositing bucket. Large pieces of uncombusted material were not included in the samples to prevent sample bias.

At the end of the sampling period, the material in the compositing bucket was thoroughly mixed with a hand trowel. The time-composite sample was placed into clean, labeled sample containers (i.e., one 1-quart glass wide-mouth jar each for PCDD/PCDF, PCB, and metals) using a steel hand trowel. In addition, the polyethylene bottle used to measure the 550-milliliter aliquots was filled to obtain the bottom/fly ash composite sample for laboratory leachate testing. The laboratory leachate composite was prepared such that it is representative of both combustors and both shifts of operation during which sampling was performed. The samples were documented on chain-of-custody forms, packed in Igloo-type coolers without ice, and shipped to the laboratory by priority air express. The coolers were sealed with EPA custody seals.

Fly ash - Similar to the bottom/fly ash samples, four time composite fly ash samples were collected composed of eight grab samples each representing each combustor/shift combination (i.e., Unit 1 or Unit 2, 2nd shift or 3rd shift). The fly ash samples were taken at the same frequencies as the bottom/fly ash samples during the 2nd and 3rd shifts. The volume of the fourth grab sample from Unit 2 was half the usual amount, because Unit 2 was running cold. Per sampling plan requirements, the fly ash time-composite collected from Unit 1 during the 2nd shift was split for field and laboratory quality control.

Each fly ash grab sample from Unit 1 was collected from a screw conveyor and each fly ash grab sample from Unit 2 was collected at the inlet to a turbulator. For each unit, screw conveyors transport the fly ash from separate cyclone separators and electrostatic precipitators to turbulators where water is added. The fly ash slurry feeds to the quench tank displacing some quench water.

The grab samples from Unit 1 were collected by placing a steel hand trowel under the discharge of the screw conveyor and collecting a full-stream cut (ASTM Method D2234-76). The full-stream cut was collected by placing the steel hand trowel under the screw conveyor discharge, allowing it to fill up, transferring the material to a polyethylene lined three-gallon bucket and repeating several times until sufficient material was collected.

The grab samples from Unit 2 were collected by placing a steel hand trowel under the inlet of the turbulator. The part-stream cut (ASTM Method D2234-76) was collected by placing the steel hand trowel under the turbulator inlet, allowing it to fill up, transferring the material to a polyethylene lined three-gallon bucket, and repeating several times until sufficient material was collected.

After each grab sample was collected, the sample was thoroughly mixed with the steel hand trowel, and a 550-milliliter aliquot (1100-milliliters for samples to be split) measured into a polyethylene bottle and poured into a covered and lined 3-gallon compositing bucket until the end of the shift.

At the end of the compositing period, the material in the compositing bucket was homogenized identically to the bottom/fly ash and placed into clean, labeled sample containers (i.e., one 1-quart glass wide-mouth jar each for PCDD/PCDF, PCB, and metals). In addition, the polyethylene bottle used to measure the 550 milliliter aliquots was filled to obtain the fly ash composite sample for laboratory leachate testing. The laboratory leachate composite was prepared such that it is representative of both combustors and both shifts of operation during which sampling was performed. Per sampling plan requirements, the laboratory leachate was split for field and laboratory control. The samples were documented on chain-of-custody forms, packed in Igloo-type coolers without ice, and shipped to the laboratory by priority air express. The coolers were secured with EPA custody seals.

Quench water - The quench water samples were grab samples representing one combustor (i.e., Unit 1 or Unit 2). The samples were collected during the second shift (i.e., Unit 1 quench water collected about half way through the shift and Unit 2 quench water collected towards the end of the shift). This being the case, these samples were not representative of the entire shift, but only the instant in time at which they were collected. Therefore, any time dependent variability of the quench water contaminant concentrations was not accounted for in these samples.

The quench water samples were collected in the tank. The fly ash slurry from the turbulator feeds to the quench tank displacing some quench water. The displaced quench water overflows to a sump where solids are removed. The effluent from the sump is discharged to the sanitary sewer. The quench water samples were collected in the tank rather than at the sump overflow because the sump overflow was not accessible.

The quench water grab samples were collected using a clean sample container (i.e., 4-oz. glass for TOC, 1-L polyethylene for metals, 1-L glass for organic scan, four 1-L glass for base/neutral/acid, two 1-L glass for PCB, and four 1-L glass for PCDD/PCDF). The samples were treated with the appropriate preservative (i.e., sulfuric acid for TOC and organic scan, and nitric acid for metals), documented on chain-of-custody forms, packed on ice in Igloo-type coolers, and shipped to the laboratory by priority air express. The coolers were secured with EPA custody seals.

### 3.3.2 Facility B

Versar personnel collected groundwater samples at Facility B's landfill on September 27, 1986, and MWC residue samples at Facility B on September 28 and 29, 1986. The MWC residue samples included: bottom ash, fly ash, and quench water. Per sampling plan, 25 percent of the samples were collected in duplicate for quality control (QC).

The MWC residue sampling at Facility B was performed during the second shift (i.e., 7:00 a.m. to 3:00 p.m.) on Sunday, September 28, 1986 and the third shift (i.e., 3:00 p.m. to 11:00 p.m.) on Monday, September 29, 1986. The reason for the length of time between each sampling shift was to determine if any differences exist in the characteristics of the residues due to the length of time the refuse has been in the incoming refuse collection pit. During sampling, Unit 2 was down for maintenance; therefore, all MWC residue samples were collected from combustion Units 3 and 4. Units 3 and 4 were sampled separately to determine if any differences exist in the characteristics of the residues due to different operating parameters and incinerator design features.

Although the Versar monitoring team also attempted to collect a field leachate sample, no natural leachate seeps were available for collection. However, at the request of EPA/HWERL, a follow-up visit was scheduled for October 22, 1986, to attempt collection of a field leachate sample. The follow-up visit was scheduled after periods of heavy rain; therefore, Versar personnel were able to collect three field leachate samples during this visit.

While the samples were being collected, the combustor operator recorded pertinent operating data to be used for evaluating contaminant concentration differences between units, shifts, and facilities (See Section 5.0). This operating data is shown in Second 4.1, Table 4.2. Table 3.5 presents a summary, including field sample numbers, of the samples collected at this facility. Detailed descriptions of the sampling locations and procedures for each of the sample matricies are presented below.

Groundwater - The groundwater samples were grab samples collected the afternoon of September 27, 1986. There are four groundwater monitoring wells at the landfill. The two wells closest to the active

TABLE 3.5 SAMPLE IDENTIFICATION CODES FOR FACILITY B

| Sample Matrix | Sample Description | TOC No. | Organic Scan No. | Metals No. | BNA No. | PCB No. | PCDD/ PCDF No. | Lab Leachate No. |
|---|---|---|---|---|---|---|---|---|
| Blank | Trip Blank | 17696 | 17698 | 17697 | 17699-02 | 11703-04 | 17705-08 | |
| Bottom | Composite | | | | | | | 17694 |
| Bottom | Unit 3, 9/28, AM | | | 17664 | | 17666 | 17665 | |
| Bottom | Unit 3, 9/29, PM | | | 17688 | | 17690 | 17689 | |
| Bottom | Unit 4, 9/28, AM | | | 17673 | | 17674 | 17675 | |
| Bottom | Unit 4, 9/28, AM, Dup | | | 17676 | | 17677 | 17678 | |
| Bottom | Unit 4, 9/29, PM | | | 17682 | | 17683 | 17684 | |
| Fly | Composite | | | | | | | 17695 |
| Fly | Unit 3, 9/28, AM | | | 17667 | | 17669 | 17668 | |
| Fly | Unit 3, 9/28, AM, Dup | | | 17670 | | 17672 | 17671 | |
| Fly | Unit 3, 9/29, PM | | | 17691 | | 17693 | 17692 | |
| Fly | Unit 4, 9/28, AM | | | 17679 | | 17680 | 17681 | |
| Fly | Unit 4, 9/29, PM | | | 17685 | | 17686 | 17687 | |
| Leachate | East Side | 19830 | 19832 | 19831 | 19833-36 | 19837-38 | 19839-42 | |
| Leachate | North Side | 19856 | 19858 | 19857 | 19861-64 | 19859-60 | 19865-68 | |
| Leachate | Northeast Corner | 19843 | 19845 | 19844 | 19848-51 | 19846-47 | 19852-55 | |
| MWell | #2 | 18367 | 17512 | 18373 | 17579-80* | | 17582-85* | |
| Quench | Unit 3, 9/28 | 18376 | 17509 | 17502 | 17588-91 | 17596-97 | 17592-95* | |
| Quench | Unit 4, 9/28 | 18377 | 17510 | 17503 | 17598-01 | 17606-07 | 17602-05 | |
| Quench | Unit 4, 9/28, Dup | 18364 | 17508 | 18371 | 17528-31 | 17536-37 | 17532-35 | |

LEGEND:

Bottom = Bottom ash
Fly = Fly ash
MWell = Groundwater from monitoring well
Quench = Incinerator quench water
TOC = Total organic carbon
BNA = Base/neutral acid extractable organics
* = Samples collected but not analyzed

area of the landfill were in poor condition (one had been damaged by a vehicle) and were dry. The two wells closest to the older portion of the landfill contained water, but one well casing was at a very steep angle and an accurate reading could not be obtained for the depth of the water surface.

Prior to sampling the groundwater in the one remaining well, the volume of standing water in the well casing and saturated annulus was determined by measuring and recording the well casing diameter, the depth from the top of the well casing to the water surface, and the depth from the top of the well casing to the sediment/water interface. The volume of standing water was approximately 2.6 gallons.

Because of the small volume of water and uncertainty on the recharging rate, the monitoring well was not evacuated. Instead, grab samples were collected from the standing water using Teflon bailers. The water was clear with no visible particulate matter; therefore, the samples were not filtered. The clean labeled sample containers (i.e., 4-oz. glass for TOC, 1-L polyethylene for metals, 1-L glass for organic scan, one and three quarter 1-L glass for base/neutral/acid, and four 1-L glass for PCDD/PCDF) were filled directly from the Teflon bailer, documented on chain-of-custody forms, packed on ice in an Igloo-type cooler, and shipped to the laboratory by priority air express. The coolers were sealed with EPA custody seals.

The Versar monitoring team returned to the Facility B landfill on September 28, 1986, to determine how well the monitoring well recharged. Unfortunately, the volume of standing water had not increased significantly, so no more samples were taken.

Bottom ash - The bottom ash samples were composite samples composed of four grab samples representing each combustor/shift combination (i.e., Unit 3 or Unit 4, 2nd shift on September 28, 1986 or 3rd shift on September 29, 1986). Unit 4 was running below optimum temperature during the beginning of the third shift on September 29, 1986. A grab sample portion of the composite was collected each time bottom ash was transferred to a dump truck during the shift. Per sampling plan requirements, the composite collected from Unit 4 during the second shift on September 29, 1986 was split for field and laboratory quality control.

Each bottom ash grab sample was collected from a disposal trailer. The bottom ash is spray quenched, stored in an enclosed hopper, and discharged into a disposal trailer about every two hours. Each trailer has sufficient capacity to hold two bottom ash dumps. During the sampling visit, Unit 3 was dumped in the back half of the trailer and Unit 4 was dumped in the front half.

The grab sample portion of the composite sample was collected by climbing up on the trailer and scooping with a steel hand trowel several aliquots of ash from the freshly dumped mound and placing the material in a polyethylene lined three-gallon collection bucket. The sample was thoroughly mixed with the steel hand trowel, and a 1-quart aliquot (2-quart for the sample to be split) was transferred into a polyethylene covered and lined 3-gallon compositing bucket until the end of the shift. Large pieces of uncombusted material were not included in the samples to prevent sample bias.

At the end of the sampling period, the material in the compositing bucket was thoroughly mixed with a hand trowel. The composite sample was placed into clean, labeled sample containers (i.e., one 1-quart glass wide-mouth jar each for PCDD/PCDF, PCB, and metals (using a steel hand trowel. The polyethylene bottle used to measure the 1-quart aliquots was filled to obtain the bottom ash composite sample for laboratory leachate testing. The laboratory leachate composite was prepared such that it is representative of both combustors and both shifts of operation during which sampling was performed. The samples were documented on chain-of-custody forms, packed in Igloo-type coolers without ice, and shipped to the laboratory by priority air express. The coolers were sealed with EPA custody seals.

Fly ash - Similar to the bottom ash samples, the fly ash samples were composites composed of four grab samples representing each combustor/shift combination (i.e., Unit 3 or Unit 4, 2nd shift on September 28, 1986, or 3rd shift on September 29, 1986). An incremental sample portion of the composite was collected at times corresponding to periods when bottom ash was dumped during the shift. Per sampling plan requirements, the composite collected from Unit 3 during the second shift on September 29, 1986, was split for field and laboratory quality control.

Each fly ash grab sample was collected from a screw conveyor. The fly ash from each unit is removed from the flue gas stream in separate cyclones and electrostatic precipitators, mechanically conveyed (i.e., screw conveyors) to a combined duct, and discharged to an enclosed storage bin through a large hose.

The grab samples were collected by turning the screw conveyor off, removing the screw conveyor cover, and collecting the exposed material with a gloved hand. The collected material was placed in a polyethylene lined three-gallon bucket.

After each grab sample was collected, the sample was thoroughly mixed with the steel hand trowel, and a 1-quart aliquot (2-quart for a sample to be split) transferred to a polyethylene bottle and poured into a polyethylene covered and lined 3-gallon compositing bucket until the end of the shift.

At the end of the compositing period, the material in the compositing bucket was homogenized and placed into clean, labeled sample containers (i.e., one 1-quart glass wide-mouth jar each for PCDD/PCDF, PCB, and metals). In addition, the polyethylene bottle used to measure the 1-quart aliquots was filled to obtain the fly ash composite sample for laboratory leachate testing. The laboratory leachate composite was prepared such that it is representative of both combustors and both shifts of operation during which sampling was performed. The samples were documented on chain-of-custody forms, packed in Igloo-type coolers without ice, and shipped to the laboratory by priority air express. The coolers were sealed with EPA custody seals.

Quench water - The quench water samples were grab samples representing one combustor (i.e., Unit 3 or Unit 4). The samples were collected during the second shift on September 28, 1986 (i.e., Unit 4 quench water collected at the beginning of the shift and Unit 3 quench water collected about half way through the shift). This being the case, these samples were not representative of the entire shift, but only the instant in time at which they were collected. Therefore, any time dependent variability of the quench water contaminant concentrations was not accounted for in these samples. Per sampling plan requirements, the grab samples for Unit 4 were split for field and laboratory quality control.

The quench water grab samples were collected below the bottom ash clamshell load-out hoppers. The bottom ash is spray quenched and stored in an enclosed hopper. Quench water drains from the bottom ash hoppers, spills to the pavement below, and is collected in a surface drain. The quench water is discharged to the sanitary sewer after solids are removed in a sump. The quench water samples were collected below the bottom ash hopper because the sump overflow was not accessible.

The quench water grab samples were collected using a 2-1/2 gallon wide-mouth glass jar. The 2-1/2 gallon jar was filled several times to obtain sufficient volume for analysis (i.e., 3 times for Unit 4 and 2 times for Unit 3). The contents of the 2-1/2 gallon jar was poured into clean labeled sample containers (i.e., 4-oz. glass for TOC, 1-L polyethylene for metals, 1-L glass for organic scan, four 1-L glass for base/neutral/acid, two 1-L glass for PCB and four 1-L glass for PCDD/PCDF). The samples were treated with the appropriate preservative (i.e., sulfuric acid for TOC and organic scan, and nitric acid for metals), documented on chain-of-custody forms, packed on ice in Igloo-type coolers, and shipped to the laboratory by priority air express. The coolers were secured with EPA custody seals.

Field leachate - Three field leachate samples were collected during the follow-up visit to Facility B on October 22, 1986. These field leachates were grab samples collected from the northeast corner and the north and east sides of the landfill. All three of these samples were collected along the bottom edge of the landfill, where natural leachate seeps flowed out from underneath the landfill. The seeps then flowed through a culvert, underneath the road, into a nearby river. The discharge point of the leachate seeps into the river was observed without noting any deleterious effects.

The natural seep streams at all three sampling locations were too shallow to collect a representative sample without disturbing the sediment. Therefore, the Versar monitoring team used a shovel to dig a sample collection basin in the leachate stream flow channel. Before the samples were collected, the leachate stream was allowed to fill the basin, and the sediment was allowed to settle. After the leachate filled the basin and was clarified, the samples were collected using a borosilicate glass beaker and transferred to the appropriate, precleaned sample containers. Then, the samples were labeled, documented on chain-of-custody forms, packed in coolers, iced, and shipped to the laboratory by priority air express.

### 3.3.3 Facility C

Versar personnel collected MWC residue samples at Facility C between September 28, 1986, and September 30, 1986. These samples included: bottom/fly ash (i.e., a mixture of bottom ash and three discrete fly ash fractions), fly ash (i.e., a mixture of the three discrete fly ash fractions), quench water, coarse fly ash (i.e., economizer ash), medium fly ash (i.e., cooling chamber ash), fine fly ash (i.e., electrostatic precipitator dust), disposed ash, and ground water (i.e., water from the facility's production well). Per sampling plan requirements, 25 percent of these samples were collected in duplicate for quality control (QC) purposes.

The sampling plan for this facility stipulated that Versar personnel would also collect field leachate and additional ground water samples. However, the Versar monitoring team was unable to obtain these samples during this visit. Although evidence of a natural leachate seep was observed below the landfill, it was dry. Nevertheless, the Versar monitoring team did observe some surface water runoff (i.e., possibly field leachate) from the landfill, but the runoff stream was extremely shallow with a minimal flow volume. Therefore, adequate sample volumes (approximately three gallons would be required) could not be collected. Furthermore, because of the extremely shallow depth of the runoff stream, a representative sample could not be collected without disturbing the sediment (i.e., disposed ash) over which the runoff was flowing.

The additional groundwater samples were to be collected from three on-site monitoring wells. However, two of these wells were locked, and all three wells were equipped with dedicated compressed air pumps (i.e., Well Wizards). The Versar monitoring team was unable to gain access to the keys or the pump operating equipment, and as a result, the wells were not sampled.

However, at the request of EPA/HWERL, a follow-up visit was scheduled for October 21, 1986, to obtain the field leachate and monitoring well samples. Prior to the follow-up visit, Versar contacted the facility's monitoring well installation and sampling contractor to ensure that the keys and pumping equipment would be available for sampling. Therefore, the three ground water samples were collected during this follow-up visit. Furthermore, because the follow-up visit was scheduled after a period of heavy rain, Versar was also able to collected three field leachate samples.

The MWC residue sampling at Facility C commenced during the second shift (i.e., 3:00 p.m. to 11:00 p.m.) on September 28, 1986, and was completed at the end of the second shift on September 30, 1986. During these sampling activities, Unit 1 was down for maintenance; therefore, all MWC residue samples were collected from combustion Unit 2. While the samples were being collected, the incinerator operator recorded pertinent operating data to be used for evaluating contaminant concentration differences between shifts and facilities (see Section 5.0). This operating data is shown in Section 4.1, Table 4.3. Table 3.6 presents a summary, including field sample numbers, of the samples collected at this facility. Detailed descriptions of the sampling locations and procedures for each of the sample matricies are presented below.

Bottom/fly ash - The Versar monitoring team had to collect a combined ash (i.e., bottom and fly ash mixture) rather than a bottom ash sample because a discrete bottom ash sampling location was not available. The bottom/fly ash sample included all the ash types generated by the facility (i.e., bottom ash, coarse fly ash, medium fly ash, and fine fly ash). These bottom/fly ash samples were time-composited samples representing one shift of operation and one combustion unit (i.e., Unit 2). Initially, the discrete grab sample portions of the composite were collected each hour over an eight-hour period, and then manually composited at the end of this period. However, because of the time required to composite and containerize (including chain-of-custody documentation, labeling, and preservation) the samples, the sampling increment was changed to every 40 minutes over a six-hour period.

Each discrete bottom/fly ash grab sample was collected from the quench water tank drag conveyor. The drag conveyor exited the quench water tank and transported the ash up an inclined surface to a load-out bin, where the ash was discharged into a truck for subsequent disposal. As the ash was conveyed up the slope, the water returned down the slope to the quench water tank. However, the ash was still very wet and contained a large amount of uncombusted material (e.g., glass, cans, metal scraps, etc.).

The sample increments were collected by stopping the drag conveyor and taking a stopped-belt cut (ASTM Method D2234-76) across the conveyor

## TABLE 3.6 SAMPLE IDENTIFICATION CODES FOR FACILITY C

| Sample Matrix | Sample Description | TOC No. | Organic Scan No. | Metals No. | BNA No. | PCB No. | PCDD/ PCDF No. | Lab Leachate No. |
|---|---|---|---|---|---|---|---|---|
| Blank | Field Blank | 19592 | | | | | | |
| Blank | Trip Blank | 19537 | 19535 | 19536 | 19525-28 | 19533-34 | 19529-32 | |
| Bottom/Fly | Composite | | | | | | | 19517 |
| Bottom/Fly | Composite, Dup | | | | | | | 19517D |
| Bottom/Fly | Unit 2, 9/28, PM | | | 19514 | | 19515 | 19516 | |
| Bottom/Fly | Unit 2, 9/29, PM | | | 19539 | | 19540 | 19541 | |
| Bottom/Fly | Unit 2, 9/30, AM | | | 19586 | | 19588 | 19587 | |
| Bottom/Fly | Unit 2, 9/30, AM, Dup | | | 19589 | | 19591 | 19590 | |
| Bottom/Fly | Unit 2, 9/30, PM | | | 19593 | | 19595 | 19594 | |
| Fly | Composite | | | | | | | 19521 |
| Fly | Unit 2, 9/28, PM | | | 19518 | | 19519 | 19520 | |
| Fly | Unit 2, 9/29, PM | | | 19542 | | 19543 | 19544 | |
| Fly | Unit 2, 9/29, PM, Dup | | | 19545 | | 19546 | 19547 | |
| Fly | Unit 2, 9/30, AM | | | 19583 | | 19585 | 19584 | |
| Fly | Unit 2, 9/30, PM | | | 19596 | | 19598 | 19597 | |
| Fly | Unit 2, Coarse | | | 19548 | | 19549 | 19550 | |
| Fly | Unit 2, Fine (ESP) | | | 19554 | | 19555 | 19556 | |
| Fly | Unit 2, Medium | | | 19551 | | 19552 | 19553 | |
| Landfill | Perimeter Composite | | | 19522 | | 19523 | 19524 | |
| Leachate | North Side | 19803 | 19829 | 19804 | 19811-14 | 19805-06 | 19807-10 | |
| Leachate | Northeast Corner | 19791 | 19828 | 19792 | 19795-98 | 19793-94 | 19799-02 | |
| Leachate | Northwest Corner | 19815 | 19827 | 19816 | 19823-26 | 19817-18 | 19819-22 | |
| MWell | #17 | 19778 | 19780 | 19779 | 19781-84 | 19785-86 | 19787-90* | |
| MWell | #3 | 19753 | 19754 | 19752 | 19755-58 | 19759-60 | 19761-64* | |
| MWell | #4 | 19766 | 19767 | 19765 | 19768-71 | 19772-73 | 19774-77* | |
| PWell | Production Well | 19581 | 19578 | 19582 | 19570-73* | 19579-80 | 19574-77* | |
| Quench | Unit 2, 9/28 | 19512 | 19511 | 19513 | 19501-04* | 19509-10 | 19505-08 | |
| Quench | Unit 2, 9/30 | 19568 | 19569 | 19557 | 19558-61 | 19566-67 | 19562-65 | |

LEGEND:

Bottom/Fly = Combined bottom ash and fly ash samples
Fly = Fly ash
MWell = Groundwater from monitoring well
PWell = Groundwater from production well
Quench = Incinerator quench water
TOC = Total organic carbon
BNA = Base/neutral acid extractable organics
* = Samples collected but not analyzed

bar using a shovel. The cut was perpendicular to the conveyor direction and was the width of the shovel. The sides of the cut were as nearly parallel as possible to prevent particle-size bias. The sample was placed in a three-gallon container and covered with polyethylene sheeting to prevent contamination during compositing.

At the end of the compositing period, the material in the bucket was poured into a polyethylene bag and thoroughly mixed by inverting the bag several times. Before the sample was containerized, large pieces of uncombusted material were removed to prevent sample bias. Then, the homogeneous material was placed into clean sample containers (i.e., one glass wide-mouth quart jar for each PCDD/PCDF, PCB, and metals sample) using a small steel garden trowel, and the samples were labeled and documented on chain-of-custody forms. An additional wide-mouth jar was filled 1/4 of the way to obtain the bottom/fly ash composite sample for laboratory leachate testing. This laboratory leachate composite sample was prepared such that it is representative of the four shifts of operation during which sampling was performed.

The four bottom/fly ash composite samples and the one bottom/fly ash laboratory leachate composite were collected during the second shifts on September 28 and 29, 1986, and the first and second shifts on September 30, 1986. Additionally, per sampling plan requirements, one of these samples (i.e., first shift on September 30, 1986) was collected in duplicate for field and laboratory quality control. The containerized samples were packed on ice in Igloo-type coolers and shipped to the laboratory by priority air express.

Fly ash - Similar to the bottom/fly ash samples, the fly ash samples were time composites representing one shift of operation and one combustion unit. Also like the bottom/fly ash samples, the fly ash sampling frequency was changed from every hour for an eight-hour period to every 40 minutes for a six-hour period. At Facility C, there were three discrete fly ash fractions that had to be collected individually and then manually composited. These three fractions were the coarse fly ash, medium fly ash, and fine fly ash.

The coarse fly ash particles settle out of the flue gas stream in the economizer. The economizer functions by forcing the flue gas through a series of bends which decrease the stream's velocity. This causes the larger particles to settle out of the stream because they become too heavy for the decreased velocity. These settled particles fall down a chute into a sloped quench water trough, where they are carried to the quench water tank.

This coarse fly ash fraction was collected at the discharge of the chute. The sample increments were collected by using a one pint container to collect a full-stream cut. The full-stream cut was collected by placing the container underneath the discharge of the chute and allowing it to fill. The sample was placed in a three-gallon bucket and covered with polyethylene sheeting to prevent contamination while the medium fly ash was being collected.

The medium fly ash particles were removed from the flue gas stream in a cooling chamber. As the flue gas enters the chamber, cooling water is sprayed on the gas stream to reduce the temperature and to remove additional fly ash particles. Then, the cooling water and ash particles descend through the cooling chamber to a small holding tank at the head of the quench water trough. Finally, the water and ash particles overflow the tank and flow down the quench water trough to the quench water tank.

This medium fly ash fraction was collected from the holding tank before it overflowed into the trough. The sample increments were collected by thoroughly mixing the contents of the holding tank with a shovel, and then removing approximately one pint of sample, using the shovel, and placing the sample in the three-gallon bucket with the coarse fly ash fraction. Again, the bucket was covered with polyethylene sheeting while the fine fly ash fraction was being collected.

The fine fly ash particles were removed from the flue gas stream in the final pollution control device, an electrostatic precipitator (ESP). The ESP comprises a series of parallel metal plates with rigid wires located between each two plates. The plates are given an electrical charge (i.e., either positive or negative), while the opposite charge is imparted to the wires. The charged wires produce coronas which charge the fine fly ash particles with the opposite charge of the plates. This causes the particles to adhere to the oppositely charged plates. The charges alternate between the wires and the plates, subsequently removing more particles. Each hour, the plates are rapped, and the adhering particles drop into a collection chamber where they are removed by a screw conveyor and carried to the quench water tank.

The fine fly ash fraction was collected from a sampling port in this screw conveyor. The sample increments were collected by removing the port cover and allowing the port to bleed for approximately one minute. Then, a one pint sample was collected using a shovel. This sampling method was analogous to the full-stream cut method used for sampling the coarse fly ash at the chute discharge. After the sample was obtained, it was placed in the compositing bucket, and the bucket was covered with polyethylene sheeting.

At the end of the compositing period, the material in the bucket was homogenized by pouring the material into a polyethylene bag and mixing. Then, the homogeneous material was placed into the clean sample containers, labeled, and documented on chain-of-custody forms. For the fly ash samples, an additional sample container was filled with 1/2 pint of the material to obtain a fly ash composite sample for laboratory leachate testing. Therefore, this sample represented the four shifts of operation during which sampling was conducted.

The four fly ash composite samples and the fly ash laboratory leachate samples were collected during the second shifts on September 28, and 29, 1986, and the first and second shifts on September 30, 1986. Per sampling plan requirements, one of these samples (i.e., second shift on September 29, 1986) was collected in duplicate for field and laboratory quality control. Three additional grab samples were also collected to more adequately characterize the fly ash. These were discrete coarse, medium, and fine fly ash samples which were collected using the procedures detailed above. These three additional samples were collected during the second shift on September 29, 1986. The containerized samples were packed on ice in Igloo-type coolers and shipped to the laboratory by priority air express.

Quench water - The quench water samples were grab samples collected in the middle of the shift. This being the case, they were not representative of the entire shift of operation, but of only the instant in time at which they were collected. Therefore, any time-dependent variability of the quench water contaminant concentrations has not been accounted for in these samples.

These quench water samples were collected from the end of a settling tank in which the quench water was clarified. As the quench water tank overflowed, the water and associated debris spilled into this settling tank. In the settling tank, the debris settled to the bottom, where it was returned to the quench water tank via a drag conveyor. At the end of the settling tank, the clarified quench water overflowed a weir into a sump. The water in the sump is pumped to the local POTW, where it is treated and discharged.

The quench water grab samples were collected at the overflow weir to the sump. A stainless steel dipper was used to collect an aliquot of the overflowing material. The dipper was passed through the overflowing stream, at a constant speed, and was not allowed to overflow. This ensured that the grab sample was representative of the entire stream and was not biased. Next, the water was poured into clean sample containers (i.e. 1-liter, amber-glass bottles with teflon- lined screw caps), and the appropriate preservative was added (i.e., nitric acid for metal samples and sulfuric acid for total organic carbon and organic scan samples). Then, the samples were labeled and documented on chain-of-custody forms. Finally, the samples were placed in Igloo-type coolers and iced to maintain the chemical and physical integrity of the samples during transport to the laboratory. These quench water samples were collected during the second shift on September 28, 1986, and during the first shift on September 30, 1986.

Production well ground water - During this first sampling visit, the Versar monitoring team was unable to collect ground water samples from the facility's monitoring wells. A grab sample was collected from the facility's production well on September 30, 1986, during the second shift.

This ground water grab sample was collected from a tap at the facility. First, the tap was fully opened and allowed to discharge for approximately two minutes to release any trapped sediments or gases. With the tap still fully opened, the amber-glass sample containers were filled. Then, the samples were labeled and documented on chain-of-custody forms, and the appropriate preservative, either nitric or sulfuric acid, was added. Finally, the samples were packed in a cooler and iced for shipment to the laboratory.

Landfill perimeter composite (disposed ash) - This sample was collected on September 29, 1986, to characterize the effects of weathering on the disposed ash material. The sample was a spatial composite collected from the perimeter of the landfill and was designed to adequately represent the wide variety of disposed material. Because the landfill has been in use since 1970, the individual sample increments represented a mixture of freshly disposed material as well as older and more weathered waste residue.

The composite sample was collected using a hand-held auger to obtain two-foot core sections. The composite comprised 50 of these individual increments. The distance between sample increments was visually estimated to yield 50 sampling locations around the landfill's perimeter. Each increment was collected by drilling down two feet, removing the auger from the hole, and placing the sample core in a compositing bucket. After the 50 increments were collected, the material in the bucket was mixed by stirring with a steel garden trowel. Then, the sample was containerized, labeled, documented, and packed for shipment to the laboratory.

Blanks - Field blank and trip blank samples were prepared to ensure that the cleaning water, sample containers, and preservatives were not sources of sample contamination. The blank samples were high purity HPLC-grade water poured into the appropriate containers with the required preservatives added. This HPLC-grade water was used for field cleaning of sampling equipment. The trip blank samples were prepared at Versar, and the appropriate preservatives were added to each sample. A trip blank was prepared for each analyte of interest and was carried to the facility during sampling activities. The field blank was prepared for total organic carbon and was prepared while at the facility.

Ground-water monitoring wells - Facility C had three monitoring wells that were sampled (3, 4, and 17). All three of these wells were located hydraulically down-gradient of the disposal area between the landfill and a river. Each monitoring well was equipped with a dedicated compressed-air pump that was used for evacuation and sampling.

Prior to sampling the ground water, the depth from the top of the well casing to the water surface was measured and recorded. Then, the depth from the top of the well casing to the sediment/water interface was measured and recorded. The difference between these two measurements yielded the height of standing water in the well. This height was used to determine the volume of standing water in the well casing and saturated annulus. A volume of water equal to five times this standing water volume was pumped from the well to ensure that all water which had been in prolonged contact with the well casing or the air was removed.

After the well evacuation was completed, a grab sample was obtained for pH and conductivity analyses. Then, the ground water samples for chemical analysis were collected and placed directly into precleaned sample containers from the Teflon tubing that was attached to the pump. Because the water was clear without any visible particulate matter, filtering of the samples was not required. After being collected, the samples were labeled, documented on chain-of-custody forms, packed in an Igloo-type cooler with ice, and shipped to the laboratory by priority air express.

Field leachate Three field leachate samples were collected during the follow-up visit to Facility C. These field leachates were grab samples collected from the north side and the northeast and northwest corners of the landfill. The northwest corner sample was collected from an area where a natural leachate seep enters a small stream that flows underneath the landfill (i.e., through a culvert). The other two samples (i.e., the north side and the northeast corner) were collected from surface water runoff streams along the bottom edge of the landfill.

All three field leachate samples were collected using a borosilicate glass beaker to dip the sample and pour it into the appropriate, precleaned sample containers. At the northwest corner, sufficient standing water was available to collect the sample without disturbing the sediment. However, as previously described in the introduction to this section, the runoff streams at the north side and northeast corner were too shallow to collect a representative sample without disturbing the sediment. Therefore, the Versar monitoring team used a shovel to dig a sample collection basin in the runoff stream flow channel. Before the samples were collected, the runoff stream was allowed to fill the basin, and the sediment was allowed to settle out of the collected leachate. After the leachate had filled the basin and was allowed to clarify, the samples were collected by using the borosilicate glass beaker to dip the sample from the collection basin.

After all the samples were collected and containerized, they were labeled and documented on chain-of-custody forms. Then, they were packed in coolers, iced, and shipped to the laboratory by priority air express.

### 3.3.4 Facility D

Versar's monitoring personnel collected MWC residue samples at Facility D between October 2, 1986, and October 4, 1986. These samples included: bottom/fly ash (i.e., a mixture of bottom ash and fly ash), fly ash (i.e., a mixture of economizer ash and electrostatic precipitator ash), quench water, disposed ash (i.e., a landfill perimeter composite), and field leachate. Per sampling plan requirements, 25 percent of these samples were collected in duplicate for quality control purposes. The Versar monitoring team was unable to collect ground water samples because Facility D did not have any functional monitoring wells.

The MWC residue sampling at Facility D commenced during the first shift on October 2, 1986, and was completed at the end of the second shift on October 4, 1986. During these sampling activities, both Unit and Unit 2 were operating; however, because of the limited availability of sampling locations, the individual units could not be sampled separately. Therefore, the MWC residue samples were representative of both units operating in combination. While the samples were being collected, the incinerator operator recorded pertinent operating data to be used for evaluating contaminant concentration differences between shifts and facilities (see Section 5.0). This operating data is presented in Section 4.1, Table 4.4. Table 3.7 presents a summary, including field sample numbers, of the samples collected at Facility D. Detailed descriptions of the sampling locations and procedures for each of the sample matricies are presented below.

Bottom/fly ash - The Versar monitoring team had to collect a combined ash (i.e., bottom and fly ash mixture) sample at Facility D because a discrete bottom ash sampling location was not available. The bottom/fly ash sample included all the ash types generated by the facility (i.e., bottom ash, economizer ash, and electrostatic precipitator ash). These bottom/fly ash samples were time composites representing one shift of operation and the average of both combustion

## TABLE 3.7 SAMPLE IDENTIFICATION CODES FOR FACILITY D

| Sample Matrix | Sample Description | TOC No. | Organic Scan No. | Metals No. | BNA No. | PCB No. | PCDD/ PCDF No. | Lab Leachate No. |
|---|---|---|---|---|---|---|---|---|
| Blank | Field Blank | 19713 | | | | | | |
| Blank | Trip Blank | 19725 | 19722 | 19726 | 19714-17 | 19724-25 | 19718-21 | |
| Bottom/Fly | Composite | | | | | | | 19678 |
| Bottom/Fly | Unit 1-2, 10/3, AM | | | 19675 | | 19677 | 19676 | |
| Bottom/Fly | Unit 1-2, 10/3, PM | | | 19682 | | 19684 | 19683 | |
| Bottom/Fly | Unit 1-2, 10/4, AM | | | 19688 | | 19690 | 19689 | |
| Bottom/Fly | Unit 1-2, 10/4, AM, Dup | | | 19691 | | 19693 | 19692* | |
| Bottom/Fly | Unit 1-2, 10/4, PM | | | 19709 | | 19712 | 19711 | |
| Fly | Composite | | | | | | | 19673 |
| Fly | Composite, Dup | | | | | | | 19674 |
| Fly | Unit 1-2, 10/3, AM | | | 19667 | | 19669 | 19668 | |
| Fly | Unit 1-2, 10/3, AM, Dup | | | 19670 | | 19672 | 19671 | |
| Fly | Unit 1-2, 10/3, PM | | | 19679 | | 19681 | 19680 | |
| Fly | Unit 1-2, 10/4, AM | | | 19685 | | 19687 | 19686 | |
| Fly | Unit 1-2, 10/4, PM | | | 19706 | | 19708 | 19707 | |
| Landfill | Perimeter Composite | | | 19599 | | 19600 | 19601 | |
| Leachate | Northeast Corner | 19639 | | 19638 | 19628-31 | 19636-37 | 19632-35 | |
| Leachate | Northeast Corner, Dup | 19627 | 19625 | 19626 | 19615-18 | 19623-24 | 19619-22 | |
| Leachate | Southeast Corner | 19614 | 19612 | 19613 | 19602-05 | 19610-11 | 19606-09 | |
| Quench | Unit 2, 10/3 | 19651 | 19648 | 19652 | 19640-43 | 19649-50 | 19644-47 | |
| Quench | Unit 2, 10/3, Dup | 19664 | | 19665 | 19653-56 | 19662-63 | 19657-60 | |
| Quench | Unit 2, 10/4 | 19704 | 19702 | 19705 | 19694-97 | 19703,27 | 19698-01 | |

LEGEND:

Bottom/Fly = Combined bottom ash and fly ash samples
Fly = Fly ash
MWell = Groundwater from monitoring well
Quench = Incinerator quench water
TOC = Total organic carbon
BNA = Base/neutral acid extractable organics
* = Sample collected but not analyzed

units (i.e., Unit 1 and Unit 2). The discrete grab sample increments used to prepare the composite were collected every 40 minutes for a six-hour period.

At Facility D, bottom and fly ash were discharged into and collected in two quench water tanks, one for each combustion unit. After being quenched, the ash material was subsequently discharged onto a belt conveyor and transported to a load-out hopper, where it was loaded into a truck for haulage to the landfill. Due to the nature of the operation, the belt conveyor could not be stopped to collect unit-specific bottom/fly ash samples. Therefore, the samples had to be collected at the load-out hopper where the ash from each unit was mixed.

The sample increments were collected as the load-out hopper discharged into the truck. A shovel was used to collect a full-stream cut (ASTM Method D2234-76) of the ash material as it fell into the truck. The shovel was moved through the falling material at a uniform rate to collect a representative portion of the falling stream. This sample portion was placed in a three-gallon bucket, which was covered with polyethylene sheeting to prevent contamination during the compositing period.

At the end of the compositing period, the material in the bucket was poured into a polyethylene bag and thoroughly mixed by inverting the bag several times. Before the sample was containerized, large pieces of uncombusted material were removed to prevent sample bias. Then, the homogeneous material was placed into clean sample containers (i.e., one glass wide-mouth quart jar for each PCDD/PCDF, PCB, and metals sample) using a small steel garden trowel, and the samples were labelled and documented on chain-of-custody forms. An additional wide-mouth jar was filled 1/4 of the way to obtain the bottom/fly ash composite sample for laboratory leachate testing. This laboratory leachate composite sample was prepared in such a way that it was representative of the four shifts of operation during which sampling was performed.

The four bottom/fly ash composite samples and the one bottom/fly ash laboratory leachate composite were collected during the first and second shifts on October 3 and 4, 1986. Additionally, per sampling plan requirements, one of these samples (i.e., first shift on October 4, 1986) was collected in duplicate for field and laboratory quality control. The containerized samples were placed in Igloo-type coolers with ice and carried to the laboratory by the Versar monitoring team.

Fly ash - Similar to the bottom/fly ash samples, the fly ash samples were time composites representing one shift of operation and the average of the two combustion units. Also like the bottom/fly ash samples, the fly ash samples were collected every 40 minutes over a six-hour period. However, unlike the bottom/fly ash samples, the fly ash sample increments had to be collected from each combustion unit individually. Consequently, because the operating capacities of the units were similar, equal volumes of fly ash were collected from each unit and manually composited.

Facility D generated two different fly ash fractions--coarse fly ash and fine fly ash. The coarse fly ash fraction is removed from the flue gas stream in an economizer. The economizer is simply a series of bends that decrease the flue gas velocity causing the coarse particles to settle out of the stream and fall down a chute to the quench water tank. The fine fly ash fraction is removed from the flue gas by a series of electrically charged parallel plates in the electrostatic precipitator (ESP). The fine ash particles have a static charge which causes them to be attracted to the oppositely charged plates. The charges on the plates are alternately changed from positive to negative, subsequently removing more of the oppositely charged particles. Each hour, the plates are rapped, and the adhering fine ash particles fall into a screw conveyor which carries the material to the chute where it joins the economizer ash. The fly ash sample increments were collected from sampling ports in this chute.

The sample increments were collected by using a stainless steel dipper to obtain a full-stream cut of the falling material. The sampling port cover was removed, and the dipper was inserted perpendicular to the falling stream. Because the dipper opening cross-sectional area was approximately equal to the interior cross- sectional area of the chute, it was ideal for collecting a representative unbiased cut. The dipper was held in the part and allowed to fill without overflowing. Then, the sample increment was placed in a compositing bucket, and the bucket was covered with polyethylene sheeting. This procedure was repeated for each unit collecting equal sample portions (i.e., one full dipper) from each.

At the end of the compositing period, the material in the bucket was homogenized by pouring the material into a polyethylene bag and mixing. Then, the homogeneous material was placed into precleaned sample containers, which were labeled and documented on chain-of-custody forms. Two additional 1-quart sample containers were partially filled with 1/2 pint of each shift composite fly ash to obtain duplicate fly ash composite samples, for laboratory leachate testing. Therefore, these two samples represented the four shifts of operation during which sampling was conducted.

The four fly ash composite samples and the two fly ash laboratory leachate samples were collected during the first and seconds shifts on October 3 and 4, 1986. Per sampling plan requirements, one of these samples (i.e., first shift on October 3, 1986) was collected in duplicate for field and laboratory quality control. The containerized samples were placed in Igloo-type coolers with and carried to the laboratory by the Versar monitoring team.

Quench water - The quench water samples were grab samples collected in the middle of the first shifts on October 3 and 4, 1986. Consequently, they were not representative of the entire shift of operation, but of only the instant in time at which they were collected. Therefore, any time-dependent variability of the quench water contaminant concentrations has not been accounted for by these samples.

The quench water samples were collected from the end of the quench water tank using a stainless steel dipper. Unlike the bottom/fly and fly ash samples that were representative of both combustion units, the quench water samples were representative of only Unit 2 because an adequate (based on safety considerations) sampling location was not available for Unit 1. The samples were collected by placing the dipper in the quench water tank and allowing it to fill. Then, the collected sample was split equally among the required number of precleaned sample containers (i.e., eleven 1-liter amber-glass bottles and one 4-ounce TOC bottle per sample). On October 3, 1986, a duplicate sample was collected by splitting each dipper among two complete sets of glass containers. The reason for splitting each filled dipper among the required containers was to prevent sample bias arising from each discrete grab. This procedure was repeated until all of the sample bottles were full.

After the sampling was completed, the appropriate preservative (i.e., nitric acid for metal samples and sulfuric acid for total organic carbon and organic scan samples) was added to each sample, and the containers were securely capped. Then, the samples were labeled and documented on chain-of-custody forms. Finally, the samples were placed in Igloo-type coolers and iced to maintain the physical and chemical integrity of the samples during transport to the laboratory.

Landfill perimeter composite (disposed ash) - This sample was collected October 2, 1986, to characterize the effects of weathering on the disposed ash material. The sample was a spatial composite collected from the perimeter of the landfill designed to adequately represent the wide variety of disposed material. Because the landfill has been in continuous use for several years, the individual sample increments represented a mixture of freshly disposed material as well as older and more weathered waste residue

The composite sample was collected using a hand-held auger to obtain two-foot core sections. The composite comprised 50 of these individual sections. The distance between sample increments was visually estimated to yield 50 sampling locations around the landfill's perimeter. Each increment was collected by drilling down two feet into the material, removing the auger from the hole, and placing the sample core in a compositing bucket. After the 50 increments were collected, the material was mixed by vigorously stirring with a steel garden trowel. Then, the sample was containerized, labeled, documented, and packed on ice for shipment to the laboratory.

Field leachate - Three field leachate samples were collected at Facility D on October 2, 1986. Facility D has a leachate collection system installed for the landfill, however, the system was obstructed, so no leachate could be obtained. Leachate samples were collected from natural depressions where surface water runoff and natural seeps collected along the bottom of the landfill. The field leachates were grab samples collected from two of these depressions at the southeast and northeast corners of the landfill. The sample from the northeast corner was collected in duplicate for quality control purposes.

All three field leachate samples were collected using a stainless steel dipper. The dipper was placed in the depression and allowed to fill with leachate. Then, the sample increment was split equally among the required number of precleaned sample containers (i.e., eleven 1-liter amber-glass bottles and one 4-ounce TOC bottle for the southeast corner, and twice as many containers for the duplicate samples at the northeast corner) to prevent sampling bias. This procedure was repeated until all of the samples bottles were full. The sample containers were securely capped, labeled, and documented on chain-of-custody forms. Finally, the samples were placed in coolers, iced, and personally delivered to Versar's laboratory by the field team.

Blanks - Field and trip blanks were prepared to ensure that the cleaning water, sample containers, and preservatives were not sources of sample contamination. The blank samples were high purity HPLC-grade water, which was used for field cleaning of sampling equipment, poured into the sample containers with the appropriate preservatives added. The trip blanks were prepared at Versar and were carried to the facility during sampling activities. The field blank was prepared for total organic carbon, while at the facility.

### 3.4 Sample Preparation and Analysis Procedures

The solid residue samples (e.g., fly ash, bottom ash, and disposed ash) and the liquid samples (e.g., field leachate, ground water, and quench water) that were collected from the specified facilities using the procedures detailed in Sections 3.3.1 through 3.3.4 were analyzed to determine the concentrations of various toxic metals and organic compounds. The solid samples were prepared for metal analyses using SW-846 Method 3050 (i.e., acid digestion) and for PCB analysis using modified SW-846 Method 3540 (i.e., soxhlet extraction) with a 1:1 mixture of hexane and acetone as the extraction solvent. The solid samples for PCDD/PCDF analyses were prepared according to the protocols specified in the analytical method (see Appendix B). For analytical QA purposes, 25 percent of the samples were collected in duplicate and submitted to the laboratory as "blind" field duplicates. Blanks, laboratory duplicates, spiked samples, and check standards were analyzed according to specification in the procedure and at a minimum frequency of 5 percent.

In addition to these solid and liquid samples, leachates were prepared in the laboratory from the solid residue samples and analyzed for metals and organics. The laboratory leachates were prepared from composites of the solid samples (i.e., one fly ash and one bottom ash composite per facility) by using three different extraction techniques: Extraction Procedure (EP), Toxicity Characteristics Leaching Procedure (TCLP), and Mono-filled Waste Extraction Procedure (MWEP; SW-924). These leaching procedures and the analytical methods are described in the following sections.

### 3.4.1 Laboratory Leachates

The laboratory leachate composite samples from each facility were subjected to three different leaching procedures in attempt to compare the data resulting from the use of three commonly accepted extraction methods. These leaching procedures were developed in order to standardize the extraction procedure used and to approximate natural leaching potential in the absence of field leachate composition data by determining the type and quantity of leachable chemical constituents within a solid waste. The leaching characteristics of the wastes are essential input data for designing landfills and leachate treatment facilities. Additionally, the EP and TCLP methods have regulatory significance; the leaching characteristics from these methods are used to classify a solid waste as hazardous or non-hazardous under the Resource Conservation and Recovery Act (RCRA). Conversely, the MWEP method was developed only to provide leaching characteristic information and has no regulatory significance. A summary of the conditions for these leaching procedures is provided in Table 3.8. A brief description of each leaching procedure is presented below.

Extraction Procedure (EP) - This laboratory leaching procedure was applied to composite samples of fly ash and bottom (or bottom/fly) ash from each facility. Since this procedure was developed to classify a solid waste as hazardous or non-hazardous based on predetermined hazard levels for 14 specific constituents, the analytical results from these EP-prepared residues may be used to formulate regulatory strategies and to evaluate the adequacy of current disposal practices. Therefore, the EP test procedure was followed very closely. Assuming the collected solid residue sample contained no filterable liquid (i.e., it contained only surface and interstitial moisture), the EP method was performed as follows:

1. Obtain a representative 100-gram sample of residue.
2. Crush material to <9.5 mm, if necessary.

Table 3.8. **Summary Conditions for EP, TCLP, and MWEP Methods**

| Conditions | EP (1) | TCLP (2) | MWEP (3) |
|---|---|---|---|
| Liquid:Solid Ratio | 20:1 | 20:1 | 10:1 per extraction |
| Extraction Medium | 0.5N acetic acid | 0.1N acetate buffer | Distilled/deionized water |
| pH Control | 5 | 5 | None |
| Extraction Time | 24 hours | 18 hours | 18 hours per extraction |
| Agitation Method | Tumbler | Tumbler @ 28-32 rpm | Tumbler |
| Temperature Control | 20-40 C | 19-25 C | 24-26 C |
| Particle Size | < 9.5 mm | < 9.5 mm | < 9.5 mm |
| Number of Extractions | 1 | 1 | 4, sequentially (4) |

(1) EP - Extraction Procedure (40 CFR 261, Appendix II).

(2) TCLP - Toxicity Characteristic Leaching Procedure (Revised 40 CFR 261, Appendix II).

(3) MWEP - Monofilled Waste Extraction Procedure (A Procedure for Estimating Monofilled Solid Waste Leachate Composition, Technical Resource Document SW-924, 2nd Edition).

(4) For this project, a modified MWEP method was used with two sequential extractions

3. Place sized solid residue in extractor vessel.

4. Add amount of deionized water equal to 16 times the weight of the solid residue.

5. Begin agitation and measure pH.
   - 5a. If pH >5.0, adjust to 5.0 ± 0.2 with 0.5N acetic acid.
   - 5b. If pH ≤5.0, no adjustment is necessary.

6. Continue monitoring pH at specified intervals adjusting pH as required in 5a for 6 hours.

7. Agitate mixture for a total of 24 hours between 20-40°C.
   - 7a. If at the end of 24 hours the pH > 5.2, adjust to 5.0 ± 0.2 and continue agitation for an additional 4 hours.
   - 7b. If pH ≤5.2, no additional agitation is necessary.

8. Add required amount of deionized water and filter mixture using a 0.45 m membrane filter.

9. Analyze or preserve filtrate (i.e., laboratory leachate) as required.

If the residue sample contained filterable liquid, the sample was first separated into its component phases (i.e., the sample was filtered), and the above procedure was carried out on the solid phase. Then, the initial filtrate and extract from the solid phase were combined for analysis. Finally, the EP leachate was analyzed for metals, total organics (i.e., organic scan), and if the TOC results from the MWEP extract exceeded 5 mg/L, organic constituents (i.e., BNA's). As specified in the sampling plan, 25 percent of these samples were collected, prepared, and analyzed in duplicate as blind (i.e., to the analysts) QA/QC samples.

Toxicity Characteristic Leaching Procedure (TCLP) - Like the EP method, this laboratory leaching procedure was applied to composite samples of fly ash and bottom (or bottom/fly) ash from each facility. The TCLP method was developed to replace EP as the hazardous waste classification criteria under RCRA. The TCLP classification criteria are based on all Appendix VIII (40 CFR 261) constituents, including volatiles, while EP classifications are based on predetermined hazard levels for only

14 specific contaminants. Therefore, the analytical results from the TCLP-prepared extracts may be more likely to be applied to a broader range of waste types than those from the EP-prepared extracts. Assuming that the solid residue sample contained no filterable liquid, the TCLP method was performed as follows:

1. Obtain a representative 100-gram sample of residue.
2. Crush material to <9.5 mm, if necessary, and place residue in extraction vessel.
3. Determine appropriate extraction medium:
    - 3a. Weigh out 5-gram subsample of residue; reduce particle size to <1 mm, if required; place sample in a 500 ml beaker.
    - 3b. Add 96.5 ml of distilled/deionized water (ASTM Type II).
    - 3c. Stir sample vigorously for 5 minutes with magnetic stirrer.
    - 3d. Measure pH, and if pH ≤5 use Extraction Fluid 1.
    - 3e. If pH >5, add 3.5 ml 1.0N HCl; slurry for 30 seconds; heat to 50°C for 10 minutes.
    - 3f. Allow mixture to cool to room temperature and measure pH.
    - 3g. If pH ≤5, use Extraction Fluid 1, and if pH >5, use Extraction Fluid 2.
4. Add amount of extraction fluid selected in Step 3 equal to 20 times the weight of the solid residue.
5. Close extraction vessel, and agitate in rotary extractor device at 30 ± 2 rpm for 18 hours, maintaining the temperature at 22 ± 3°C.
6. Filter material through a 0.6 to 0.8 um glass fiber filter.
7. Analyze or preserve filtrate as required.

If the residue sample contained filterable liquid, the sample was first separated into its component phases, and the above procedure was carried out on the solid phase. Then, if the initial filtrate and solid extract were compatible (i.e., did not form multiple phases or precipitates upon combination), they were combined together for analysis. If these liquids were incompatible, they were analyzed separately, and the results were mathematically combined to yield the total leachable composition of the solid residue sample. Finally, the TCLP leachate was analyzed for metals, total organics (i.e., organic scan), and BNA's (i.e., if the TOC results from the MWEP extract exceeded 5 mg/L). Although not specified in the scope of work, the TCLP leachates were also analyzed for PCDD/PCDF at the request of EPA/OSW to determine whether this method would extract these hazardous organic compounds. As specified in the contract, 25 percent of these samples were collected, prepared, and analyzed in duplicate as blind QA/QC samples.

Mono-filled Waste Extraction Procedure (MWEP) - As was the case for the EP and TCLP methods, this laboratory leaching procedure was applied to composite samples of fly ash and bottom (or bottom/fly) ash from each facility. The MWEP method was developed to estimate the quantity of potentially leachable constituents in a given solid waste and to measure the concentration of these constituents in extracts produced by various solid to liquid extraction ratios. This procedure includes a sequential four-step batch extraction which produces data that can be used to construct an aqueous extraction profile for each of the constituents. For this MWC residue study, however, Versar used a modified MWEP method with only two sequential batch extractions. Unlike the EP and TCLP methods, the MWEP has no regulatory significance. The justification for using this method is its applicability to mono-filled wastes only, which was one of the facility selection criteria (See Section 3.1.1). The modified MWEP method was performed as follows:

1. Obtain subsample and determine percent solids.
2. Obtain representative sample equal to 100 grams dry weight and place in extraction vessel.
3. Add appropriate amount of distilled/deionized water to give a 10:1 liquid to solid weight ratio, taking into account the moisture determined in step one.
4. Extract (i.e., agitate using a tumbler) the mixture for 18 hours at a temperature of 25 ± 1°C.
5. Filter mixture through a 0.45 um nitrocelluse membrane filter (for inorganic analyses) or a 0.6 - 0.8 um glass fiber filter (for organic analyses).

6. **Retain filtrate for subsequent analysis. Place in properly cleaned sample container and preserve as required.**
7. **Place filter cake (i.e., solid residue) back into extraction vessel and add 1 liter of fresh distilled/deionized water.**
8. Repeat steps 4 through 6.
9. Analyze the two sequential extracts separately.

Each of the two extracts were analyzed for metals, total organics (i.e., organic scan), and total organic carbon (TOC). If the TOC concentration of either extract was greater than 5 mg/L, then the EP and TCLP extracts, as well as both MWEP extracts, were analyzed for organic constituents (i.e., BNA's). The EP and TCLP extracts were not analyzed for total organic carbon because an organic acid (i.e., acetic acid) was used for pH control during the leaching procedure. As specified in the sampling plan, 25 percent of these samples were collected, prepared, and analyzed in duplicate as blind QA/QC samples to determine the reproducibility of sampling, preparation, and analysis procedures.

### 3.4.2 Analyses

Analyses required by the Scope of Work included total organic carbon, total metals (i.e., As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, and Zn), organic scan, PCDD/PCDF, and PCB's. Additionally, the analysis of organic constituents (i.e., BNA's) was required contingent upon the results of the total organic carbon and organic scan analyses. All of these analyses were conducted using EPA-approved procedures. Table 3.9 provides the analytical methods, techniques, and detection limits for these analyses. It should be noted that although Table 3.9 gives the primary analytical method reference (e.g., SW-846 and MCAWW), the methods were applied as modified by the Contract Laboratory Program (CLP) Statement of Work for the applicable analytes (i.e., metals and BNA's). A brief description of the analytical methods used for each parameter is presented below.

Table 3.9. Summary of Analytical Methods and Detection Limits

| | Liquid Samples (1) | | | Solid Samples (2) | | |
|---|---|---|---|---|---|---|
| Parameter | Analytical Method (3) | Analytical Technique (4) | Detection Limit (5) | Analytical Method (3) | Analytical Technique (4) | Detection Limit (5) |
| Total Organic Carbon | MCAWW-415.1 | COMB/OXID | 1 mg/L | N/A | N/A | N/A |
| Organic Scan | MCAWW-418.1 | IR SPEC | 0.25 mg/L | N/A | N/A | N/A |
| Arsenic | MCAWW-206.2 | Furnace AA | 10 ug/L | SW846-7060 | Furnace AA | 1.0 mg/kg |
| Cadmium | MCAWW-200.7 | ICAP | 5 ug/L | SW846-6010 | ICAP | 0.5 mg/kg |
| Chromium | MCAWW-200.7 | ICAP | 10 ug/L | SW846-6010 | ICAP | 1.0 mg/kg |
| Copper | MCAWW-200.7 | ICAP | 25 ug/L | SW846-6010 | ICAP | 2.5 mg/kg |
| Iron | MCAWW-200.7 | ICAP | 100 ug/L | SW846-6010 | ICAP | 10 mg/kg |
| Lead | MCAWW-239.2 | Furnace AA | 5 ug/L | SW846-7421 | Furnace AA | 0.5 mg/kg |
| Manganese | MCAWW-200.7 | ICAP | 15 ug/L | SW846-6010 | ICAP | 1.5 mg/kg |
| Mercury | MCAWW-245.1 | Cold Vapor AA | 0.2 ug/L | SW846-7471 | Cold Vapor AA | 0.02 mg/kg |
| Nickel | MCAWW-200.7 | ICAP | 40 ug/L | SW846-6010 | ICAP | 4.0 mg/kg |
| Selenium | MCAWW-270.2 | Furnace AA | 5 ug/L | SW846-7740 | Furnace AA | 0.5 mg/kg |
| Zinc | MCAWW-200.7 | ICAP | 20 ug/L | SW846-6010 | ICAP | 2.0 mg/kg |
| PCDD/PCDF's | Appendix B | HRGC/HRMS | 20 ng/L | Appendix B | HRGC/HRMS | 20 ug/kg |
| PCB's | Appendix C | HRGC/EIMS | 5-50 ug/L (6) | Appendix C | HRGC/EIMS | 0.2-1 ug/kg (6) |
| Organic Constituents | ORG-625 | GC/MS | 10-50 ug/L (7) | N/A | N/A | N/A |

N/A - Not Applicable; these analyses will not be conducted on solid samples.

(1) - Liquid samples include: field leachate, quench water, ground water, and laboratory leachate.

(2) - Solid samples include: fly ash, bottom ash, disposed ash, etc. Solid samples will be prepared for metals analyses using SW-846 Method 3050--Acid Digestion.

(3) - Referenced analytical methods are from the primary sources listed below, however, these methods will be applied as modified by Contract Laboratory Program (CLP) Statement of Work for metals and organic constituents.

MCAWW = U.S. EPA, Methods for Chemical Analysis of Water and Wastes, March 1983 (EPA-600/4-79-020).

ORG = U.S. EPA, Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater, July 1982 (EPA-600/4-82-05

SW846 = U.S. EPA, Test Methods for Evaluating Solid Wastes - SW-846, April 1984.

Appendix B = Analytical Procedures to Assay Stack Effluent Samples and Residual Combustion Products for Polychlorinated Dibenzo-p-Dioxins (PCDD) and Polychlorinated Dibenzofurans (PCDF), Group C - Environmental Standards Workshop (ASME, U.S. DOE, and U.S. EPA), September 1984.

Appendix C = Method 680. Determination of Pesticides and PCBs in Water and Soil/Sediment by Gas Chromatography/Mass Spectrometry, U.S. EPA, EMSL, Cincinnati, OH, November 1985.

(4) - COMB/OXID = Combustion/Oxidation; IR SPEC = Infrared Spectrophotometric; ICAP = Inductively Coupled Argon Plasma; HRGC/HRMS = High Resolution Gas Chromatography (Capillary Column)/High Resolution Mass Spectrometry HRGC/EIMS = High Resolution Gas Chromatography/Electron Impact Mass Spectrometry; GC/MS = Gas Chromatography/Mass Spectrometry.

(5) - Detection limits are Contract Required Detection Limits (CRDLs) from CLP for metals and organic constituents.

(6) - Detection limits increase with increasing level of chlorination. Solid samples will be prepared for PCB analyses using SW-846 Method 3540--Soxhlet Extraction.

(7) - Detection limits for individual constituents are listed in the method.

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Total Organic Carbon (TOC) - Total organic carbon analysis was performed on all field water samples (i.e., field leachate, quench water, and ground water) and laboratory leachate prepared using MWEP. The results of the total organic carbon analyses were used to initiate the BNA contingency analysis. Each field water sample that had a TOC concentration of greater than 5 mg/L was analyzed for BNA's. Additionally, if either of the two MWEP extracts contained greater than 5 mg/L TOC, then the EP, TCLP, and both MWEP extracts were analyzed for BNA's.

The TOC analysis was performed by converting the organic carbon in the sample to carbon dioxide by catalytic combustion. Then, the carbon dioxide was measured using infrared detection. Prior to analyzing each batch of samples, the infrared detector was calibrated by analyzing a blank and three standards, and plotting a curve of peak area (from a strip chart recorder) versus concentration. Finally, the measured amount of carbon dioxide in the sample (i.e., the peak area) was compared to the calibration curve to determine the TOC concentration of the sample.

Organic Scan - The organic scan was performed on all field water samples and laboratory leachates to determine whether organic compounds other than PCDD's, PCDF's, and PCB's were present. The organic scan was performed by acidifying the sample to pH <2 and extracting it with fluorocarbon 113 in a separatory funnel. The extract was analyzed using an infrared spectrophotometer that was calibrated before each batch of samples using five calibration standards that bracketed the expected sample concentration. The calibration curve was constructed by plotting the absorbence of these standards versus their respective concentrations, and the organic content of the sample was determined by direct comparison of its absorbence to the standards.

Metals - Total metal analyses were performed on all field water samples, laboratory leachates, and solid samples. The solid samples and liquid samples containing particulate matter were prepared using EPA Method 3050 (SW-846), as modified by CLP, which is an acid digestion procedure. After the sample was digested, it was analyzed using the appropriate technique: Cold Vapor Atomic Absorption (Hg), Graphite Furnace Atomic Absorption (As, Pb, and Se), or Inductively Coupled Argon Plasma (Cd, Cr, Cu, Fe, Mn, Ni, and Zn).

The Cold Vapor AA technique is a flameless AA procedure based on the absorption of radiation by mercury vapor. First, the mercury was reduced to the elemental state and aerated from solution in a closed system. Then, the mercury vapor passed through a cell positioned in the light path of an AA spectrophotometer. The spectrophotometer was calibrated before each day of analysis using a blank and five mercury standards to construct a calibration curve of absorbence versus micrograms of mercury. The absorbence of the sample (i.e., peak height on a strip-chart recorder) was compared to the calibration curve to determine the mercury concentration of the sample.

The Graphite Furnace technique also used an AA spectrophotometer to determine the metal concentration. The spectrophotometer was calibrated daily before analysis for each metal by using a blank and three calibration standards that bracketed the expected sample concentration. The standards were analyzed, and internal curves of absorbence versus concentration were constructed by a microcomputer. This calibration procedure had to be performed each time a new metal was analyzed.

For Graphite Furnace AA analysis, a representative aliquot of the sample was placed in a graphite tube within the furnace, evaporated to dryness, charred, and atomized. Concurrently, energy (i.e., a beam of light at a wavelength specific to the metal of interest from a hollow cathode tube) was directed through the graphite tube containing excited energy level atoms of the vaporized metal. The intensity of the transmitted radiation was used to determine the absorbence ($A = 2 - \log \% T$), which is directly proportional to the concentration of the metal atoms contained in the vapor. This absorbence was measured, and the specific metal concentration was determined by direct comparison to standards (i.e., the internal calibration curve).

Unlike the previous two methods, the ICAP procedure can be used to measure the concentrations of several different metals, concurrently. The previous two methods can only quantify one particular metal in each sample aliquot, but they were used because they generally offer greater sensitivity (i.e., a lower detection limit).

Prior to analysis each day, the ICAP instrumentation was calibrated for each metal analyte of interest by using two blanks (i.e., calibration blank and a reagent blank) and three standards that bracketed the anticipated sample concentrations. Before analyzing these standards, the analyst entered the actual standard concentrations for each metal into the ICAP computer. Subsequently, during the analysis of the calibration standards, the computer generated initial calibration curves based on these entered concentrations and the characteristic atomic-line spectra intensities.

During ICAP analysis, the sample was reduced to a fine spray (i.e., an aerosol) and transported to a plasma torch where excitation occurred. Then, characteristic atomic-line spectra were produced for each metal present in the aspirated sample, and these spectra were dispersed by a grating spectrometer. Finally, the intensities of the dispersed metal characteristic spectral lines were compared to standards (i.e., the internal calibration curves) to yield the concentration of each metal in the sample.

PCDD/PCDF - PCDD/PCDF analyses were performed on all fly ash samples. When the results of these analyses showed concentrations of total PCDD's or PCDF's in any of the four fly ash samples from a given facility exceeding 5 ng/g, the bottom (or bottom/fly) ash samples, TCLP-prepared leachates, field leachate samples, and quench water samples from that facility were analyzed for PCDD/PCDF. The analytical method is designed to quantify the individual homologs (homolog refers to the total number of chlorine atoms in the organic structure, but not to the position of those atoms) in the tetra- through octa-chlorinated classes,

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but not to quantify the individual isomers within these classes. One notable exception was the 2,3,7,8-TCDD isomer, which was quantified. The PCDD/PCDF analyses were performed by Versar's subcontractor, Battelle Columbus Laboratories. The analytical method used by Battelle is included in this report as Appendix B.

The first step of this analytical method was a sample extraction procedure using the appropriate organic solvent(s). Next, the extract was subjected to a sequence of liquid chromatography elutions to remove co-extracted interferences. Then, the cleaned extract was introduced into a capillary column gas chromatography instrument with a high resolution mass spectrophotometer for identification and quantification of the individual constituents. Prior to analyzing for PCDD/PCDF, the GC/MS system was calibrated using three standards that bracketed the expected sample concentration range. Finally, the homologs were identified and quantified by comparison of their retention times and mass spectral intensity ratios to those of the calibration standards.

PCB's - Analysis of PCB's was performed on all fly ash samples. If the results of the PCDD/PCDF analyses triggered the analysis of bottom (or bottom/fly) ash samples, field leachates, and quench water samples from a given facility as discussed above, the contingency analyses for PCB's were also performed on these samples. Similar to the PCDD/PCDF analytical method, the PCB method was used to identify and quantify the PCB homologs, and not the individual isomers.

All field water samples were analyzed by EPA Method 680 subtitled "Determination of Pesticides and PCBs in Water and Soil/Sediment by Gas Chromatography/Mass Spectrometry." The analytical method is incorporated into this report as Appendix C.

This method was recommended by Ms. Ann Alford-Stevens of EPA Environmental Monitoring and Support Laboratory (EMSL) in Cincinnati, Ohio. Method 680 is a published, validated method for water samples only. It is the most current GC/MS analytical procedure for the determination of

PCBs identified and measured as isomer groups or homologs. Also developed with the method is a software package which automates the data reduction to the full-scan GC/MS data generated by the method.

EPA Method 680 does not provide a procedure for extraction of PCBs from solid samples, however. The Versar laboratory tested and adapted SW-846 Method 3540, a general extraction procedure, to the extraction of PCBs from fly ash and combined bottom/fly ash samples. Preliminary tests were conducted using the 20 fly ash samples from the four facilities to verify that the extraction procedure was valid. These tests and the results are described below.

- Method Tests

The method tests consisted of two trial runs of the method using a blank, a standard, and a real ash sample. The combined methods to be tested included the following steps:

1. Soxhlet extraction of the fly ash with acetone/hexane
2. Acid cleanup of the extract
3. Micro florisil column cleanup of the extract
4. Full scan GC/MS analysis of the samples
5. Data reduction using the automated software for Method 680

For the first test, the test "samples" were processed through all of the steps listed above. The results indicated a serious problem with the method. No surrogates were recovered. The problem was determined to be in the extraction process. Overall there did not seem to be any major problems with applying the analytical procedures to the samples, but the problem with surrogate recovery had to be resolved.

A second test was initiated. For the second test, the cleanup procedures, which were suspected to be the problem, were omitted. The surrogates were recovered. The analysis showed that the second test was an improvement over the first but that there were still some problems. Additional tests showed that there were losses occurring during the concentration step of the final extract. After rinsing the walls of the concentration vessel, the recoveries were much better.

After the second test is was decided to proceed with samples without the cleanup. The cleanup was suspected of contributing to the recovery deficiency, and the samples analyzed did not present an analytical problem without the cleanup.

- Fly Ash Extraction Method 3540 Summary

Samples were extracted using SW-846 Method 3540 adapted to ash samples. Twenty grams of the ash samples were weighed out. Each sample aliquot was spiked with stable labeled PCB surrogates (carbon$^{13}$ 4-chlorobiphenyl, carbon$^{13}$ 3,3'-4,4'-tetrachlorobiphenyl, carbon$^{13}$ 2,2',3,3',5,5',6,6'-octachlorobiphenyl, and carbon$^{13}$ decachlorobiphenyl). Soxhlet extraction with 1:1 acetone/hexane was performed for 16 hours.

The extract was then concentrated to a final volume of 50 ul for analysis. The following changes were made to the method: sample size was increased to 20 grams, no sodium sulfate was added to the sample during extraction, and the final volume was adjusted to 50 ul.

- Fly Ash Analysis Method 680 Summary

Samples were analyzed using U.S. EPA Method 680. Four surrogates were added to samples prior to extraction, and one internal standard was added to each extract before GC/MS analysis. The analysis was performed on a Finnigan 5100 GC/MS DS. The chromatographic column used was a Restek RTX-5 30-meter 0.32 mm-id fused silica capillary column temperature programmed from 80C to 302C at 15C per minute. Samples were injected in the splitless mode. The scan range was 45-550 amu.

Prior to analysis, the system was calibrated to FC-43 and adjusted to meet U.S. EPA calibration requirements for 10 ng of DFTPP. An initial five point calibration curve was generated by injecting 1 ul aliquots of calibration standards supplied by EMSL Cincinnati. The calibration curve was checked daily with a continuing calibration check standard before each 12-hour sequence.

PCBs were identified and measured by isomer group (homolog). The automated software utilizes characteristic mass spectral features of PCBs at each level of chlorination for identification. Additional mass spectral confirmation checks were made by chemists after the automatic selection and quantification of PCBs was completed. Adjustments to the PCB concentration were made in those instances where additional professional mass spectral interpretation disagreed with the confirmation made by the automated data reduction program. The additional checks consisted of verifying acceptable quantitation and confirmation ion ratios, presence of M-70 confirmation ion, and absence of M+70 and M+35 interfering ions.

- Detection Limits

Method 680 does not provide PCB isomer method detection limits or a method for the determination of detection limits. Due to the nature of the analysis, a rigorous method may not be possible. However, in order to better understand the meaning of the data and illustrate its limitations, estimated detection limits were derived. They are stated in the method to be in a working range of 1 ng to 10 ng. Based on this information, and the information obtained from preliminary method evaluation, Versar's best estimates for detection limits of the PCB homologs are listed below.

Estimated Detection Limits for the PCB Homologs
Using Method 680 for Fly Ash Analysis

| Isomer Group | ug/kg |
|---|---|
| Monochlorobiphenyls | 0.2 |
| Dichlorobiphenyls | 0.3 |
| Trichlorobiphenyls | 0.4 |
| Pentachlorobiphenyls | 0.6 |
| Hexachlorobiphenyls | 0.6 |
| Heptachlorobiphenyls | 0.7 |
| Octachlorobiphenyls | 0.8 |
| Nonachlorobiphenyls | 0.9 |
| Decachlorobiphenyl | 1.0 |

The fly ash samples were extracted in two separate groups consisting of samples from Facilities A and B, and from Facilities C and D, respectively. Extraction of the first group was begun on November 13, and completed on November 17, 1986. The remaining ash samples were extracted November 18 through November 20.

Sodium sulfate was initially omitted from the extraction process. No problems were observed during the method development from this modification. The extracts from the first group of samples (extracted November 13) resulted in the formation of two layers upon concentrating. In some instances, these layers could both be organic resulting in partitioning of the analyte. In addition, distinct layers in the extract could be a result of water. Sodium sulfate was, therefore, incorporated into all further extractions. An equal weight of sodium sulfate was added to the soxhlet extractor; in addition, the extract was poured through a sodium sulfate column into the Kuderna-Danish (KD) flask.

The low surrogate recoveries of the carbon 13 monochlorobiphenyl and tretrchlorobiphenyl for the extractions dated November 13 were a result of the final concentration step. The extract was transferred from the ampule to a 1 ml conical vial. The ampule was rinsed with 10 1 ml aliquots. Each rinse aliquot was blown down with nitrogen gas in a 1 ml conical vial. This probably resulted in the loss of lighter molecular weight (higher vapor pressure) congeners. As a result, a 5-ml conical vial was used instead of the 1 ml vial. In addition, an emphasis was placed on passing a gentle stream of nitrogen over the extract. Precipitation of crystals during the concentration step presented a potential problem with the absorption of the analyte to the crystalline particulates. To alleviate this problem, the extract was passed through a micro sodium sulfate column during the concentration. The columns were rinsed thoroughly with hexane to minimize the loss of the analyte.

Incorporating the modifications discussed, the technique used in all extractions after November 13 was as follows. The extract was concentrated to approximately 10 ml in a KD flask. The extract and rinsings were passed through a pipette containing sodium sulfate into a 50 ml centrifuge tube. The extract was gently blown to 3 ml. If the precipitation of particulates occurred again, an additional filtering was performed. The extract was then transferred to a 5 ml conical vial and gently concentrated to 50 ul. During concentration, the sides of the vial were rinsed thoroughly. Once concentrated to 50 ul, the vial was centrifuged to ensure the viscous extract collected exclusively at the bottom of the conical vial.

Organic Constituents (BNA's) - The analysis for BNA's was performed on field water samples (i.e., quench water, ground water, and field leachates) and laboratory leachates contingent upon the results of the TOC and organic scan analyses. If the TOC and/or organic scan results exceeded 5 mg/L for any of these samples, then, the sample was also analyzed for BNA's.

Prior to initiating calibration or analysis, the standard mass spectral abundance criteria were established for the GC/MS system. This was accomplished by analyzing a 50 ng injection of decafluorotriphenylphosphene (DFTPP) and tuning the system as necessary. The criteria were demonstrated daily or for each twelve-hour period of operation, whichever was more frequent. After the tuning criteria were established by using DFTPP, but prior to initiating sample analysis, the GC/MS system was initially calibrated using five standards that contained all the required compounds.

The organic constituents were determined by extracting the samples with methylene chloride using a continuous extractor, and analyzing the extract using gas chromatography/mass spectrometry (GC/MS). The individual organic constituents were identified and quantified using retention times and extracted ion current profiles.

## 4.0 RESULTS AND DISCUSSION

After the laboratory analyses were completed as detailed in Section 3.4, the analytical results were summarized by sample matrix, analytical parameter, and facility. These summaries include: the facility operating parameters during sampling; the analytical results of each sample, including blanks; averages and standard deviations of each analytical parameter by sample matrix and facility; and QC data, including relative percent differences (RPDs) for each set of "blind" field duplicate and laboratory duplicate samples and recoveries for spiked samples. These summary tables were evaluated to determine any significant trends in the data between facilities, sample types (i.e., matrices ), shifts, and combustion units. The summary tables and evaluations are presented in the following sections.

### 4.1 Facility Operating Parameters

During the sampling activities at each facility, the incinerator operator recorded hourly operating parameters. These operating parameters were collected to determine whether differences in the parameters significantly affect the MWC residue composition. The operating data were used in an attempt to explain significant differences between shifts of operation, combustion units, and/or facilities (see Section 5.3). Tables 4.1, 4.2, 4.3, and 4.4 provide the operating parameters for Facilities A, B, C, and D, respectively.

These tables include the unit, date, shift, time, feed rate, ram speed (related to feed rate), probe temperature, steam production rate, combustion air, and electrostatic precipitator (ESP) specifications. The unit refers to the combustion unit number from which the samples were collected, while the date and shift refer to the date and shift of operation during which the samples were collected. The time indicates when the operating parameters were recorded. The next parameter on the table, feed rate, is expressed as both buckets and tons. The buckets indicate the number of feed crane loads that were fed into the charging

## TABLE 4.1 SUMMARY OF FACILITY A OPERATING PARAMETERS

| Unit | Date | Shift | Time | Feed Rate | | Ram Speed | Probe Temp. | Steam | Combustion Air | | ESP (Outlet) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | (Buckets) | (tons) | (Units) | (F) | (lb/hr) | Total (Units) | Overfire (Units) | (Kv) | (mA) |
| 1 | 9/26 | AM | 700 | 5 | 3.5 | 40 | 1,000 | 26,000 | 50 | NA | 24 | 160 |
| 1 | 9/26 | AM | 800 | 4 | 2.8 | 40 | 980 | 23,000 | 50 | NA | 24 | 160 |
| 1 | 9/26 | AM | 900 | 5 | 3.5 | 30 | 1,100 | 32,000 | 65 | NA | 26 | 200 |
| 1 | 9/26 | AM | 1000 | 5 | 3.5 | 45 | 1,000 | 28,000 | 65 | NA | 24 | 120 |
| 1 | 9/26 | AM | 1100 | 5 | 3.5 | 50 | 1,020 | 30,000 | 65 | NA | 26 | 120 |
| 1 | 9/26 | AM | 1200 | 6 | 4.2 | 35 | 1,060 | 32,000 | 65 | NA | 26 | 240 |
| 1 | 9/26 | AM | 1300 | 5 | 3.5 | 30 | 1,080 | 30,000 | 65 | NA | 26 | 240 |
| 1 | 9/26 | AM | 1400 | 5 | 3.5 | 50 | 1,020 | 28,000 | 65 | NA | 28 | 320 |
| | | | TOTAL | 40 | 28 | NA | NA | 229,000 | NA | NA | NA | NA |
| | | | AVERAGE | NA | NA | 40 | 1,033 | 28,625 | 61 | NA | 26 | 195 |
| 1 | 9/26 | PM | 1500 | 6 | 4.2 | | | | | | | |
| 1 | 9/26 | PM | 1600 | 5 | 3.5 | 20 | 920 | 28,000 | 70 | NA | 22 | 130 |
| 1 | 9/26 | PM | 1700 | 5 | 3.5 | 0 | 800 | 15,000 | 0 | NA | 23 | 110 |
| 1 | 9/26 | PM | 1800 | 4 | 2.8 | 0 | 410 | 5,000 | 0 | NA | 22 | 110 |
| 1 | 9/26 | PM | 1900 | 4 | 2.8 | 30 | 850 | 27,000 | 70 | NA | 22 | 130 |
| 1 | 9/26 | PM | 2000 | 3 | 2.1 | 30 | 750 | 20,000 | 70 | NA | 25 | 140 |
| 1 | 9/26 | PM | 2100 | 4 | 2.8 | 20 | 1,110 | 29,000 | 70 | NA | 26 | 140 |
| 1 | 9/26 | PM | 2200 | 0 | 0 | 40 | 940 | 25,000 | 70 | NA | 23 | 100 |
| | | | TOTAL | 31 | 21.7 | NA | NA | 149,000 | NA | NA | NA | NA |
| | | | AVERAGE | NA | NA | 20 | 826 | 21,286 | 50 | NA | 23 | 123 |
| 2 | 9/26 | AM | 700 | 4 | 2.8 | 10 | 1,100 | 24,000 | 28 | 40 | 28 | 400 |
| 2 | 9/26 | AM | 800 | 5 | 3.5 | 15 | 1,080 | 26,000 | 28 | 40 | 24 | 300 |
| 2 | 9/26 | AM | 900 | 4 | 2.8 | 15 | 1,080 | 23,000 | 28 | 40 | 30 | 440 |
| 2 | 9/26 | AM | 1000 | 3 | 2.1 | 10 | 1,200 | 26,000 | 28 | 40 | | |
| 2 | 9/26 | AM | 1100 | 4 | 2.8 | 15 | 1,060 | 23,000 | 28 | 40 | 28 | 450 |
| 2 | 9/26 | AM | 1200 | 3 | 2.1 | 10 | 1,040 | 23,000 | 28 | 40 | 28 | 260 |
| 2 | 9/26 | AM | 1300 | 4 | 2.8 | 20 | 1,040 | 22,000 | 28 | 40 | 30 | 460 |
| 2 | 9/26 | AM | 1400 | 4 | 2.8 | 5 | 1,200 | 28,000 | 28 | 40 | 28 | 240 |
| | | | TOTAL | 31 | 21.7 | NA | NA | 195,000 | NA | NA | NA | NA |
| | | | AVERAGE | NA | NA | 12.5 | 1,100 | 24,375 | 28 | 40 | 28 | 364 |
| 2 | 9/26 | PM | 1500 | 4 | 2.8 | | | | | | | |
| 2 | 9/26 | PM | 1600 | 4 | 2.8 | | 1,120 | 28,000 | 30 | 0 | 25 | 250 |
| 2 | 9/26 | PM | 1700 | 5 | 3.5 | 20 | 1,300 | 35,000 | 28 | 0 | 28 | 420 |
| 2 | 9/26 | PM | 1800 | 3 | 2.1 | 10 | 1,000 | 26,000 | 30 | | 28 | 380 |
| 2 | 9/26 | PM | 1900 | 5 | 3.5 | 15 | 1,020 | 22,000 | 30 | | 29 | 220 |
| 2 | 9/26 | PM | 2000 | 4 | 2.8 | 30 | 1,050 | 28,000 | 32 | | 24 | 220 |
| 2 | 9/26 | PM | 2100 | 6 | 4.2 | 10 | 1,080 | 24,000 | 32 | | 28 | 220 |
| 2 | 9/26 | PM | 2200 | 0 | 0 | 20 | 1,110 | 27,000 | 30 | | 30 | 350 |
| | | | TOTAL | 31 | 21.7 | NA | NA | 190,000 | NA | NA | NA | NA |
| | | | AVERAGE | NA | NA | 17.5 | 1,097 | 27,143 | 30 | 0 | 27 | 294 |

## TABLE 4.2 SUMMARY OF FACILITY B OPERATING PARAMETERS

| | | | | Feed Rate | | | Probe | | Combustion Air | | ESP | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Unit | Date | Shift | Time | (Buckets) | (tons) | Ram Speed (Units) | Temp. (F) | Steam (lb/hr) | Total (Units) | Overfire (Units) | Zone #1 (mA) | Zone #2 (mA) |
| 3 | 9/28 | AM | 800 | 19 | 13.3 | 34 | 1,650 | 80,000 | 45 | 27 | 89 | 107 |
| 3 | 9/28 | AM | 1000 | 19 | 13.3 | 34 | 1,450 | 80,000 | 30 | 27 | 89 | 107 |
| 3 | 9/28 | AM | 1200 | 19 | 13.3 | 35 | 1,500 | 80,000 | 45 | 24 | 89 | 107 |
| 3 | 9/28 | AM | 1400 | 19 | 13.3 | 35 | 1,350 | 80,000 | 45 | 23 | 89 | 107 |
| | | | TOTAL | 76 | 53.2 | NA | NA | 320,000 | NA | NA | NA | NA |
| | | | AVERAGE | NA | NA | 34.5 | 1,488 | 80,000 | 41 | 25 | 89 | 107 |
| 3 | 9/29 | PM | 1600 | 19 | 13.3 | 25 | 1,425 | 80,000 | 20 | 20 | 89 | 107 |
| 3 | 9/29 | PM | 1800 | 19 | 13.3 | 28 | 1,300 | 80,000 | 55 | 26 | 89 | 107 |
| 3 | 9/29 | PM | 2000 | 19 | 13.3 | 34 | 1,250 | 76,000 | 100 | 19 | 89 | 107 |
| 3 | 9/29 | PM | 2200 | 19 | 13.3 | 33 | 1,400 | 84,000 | 50 | 19 | 89 | 107 |
| | | | TOTAL | 76 | 53.2 | NA | NA | 320,000 | NA | NA | NA | NA |
| | | | AVERAGE | NA | NA | 30 | 1,344 | 80,000 | 56 | 21 | 89 | 107 |
| 4 | 9/28 | AM | 800 | 21 | 14.7 | 24 | 1,250 | 99,000 | | 22 | 56 | 104 |
| 4 | 9/28 | AM | 1000 | 21 | 14.7 | 22 | 1,303 | 100,000 | | 22 | 48 | 104 |
| 4 | 9/28 | AM | 1200 | 21 | 14.7 | | 1,345 | 99,000 | | 22 | 48 | 104 |
| 4 | 9/28 | AM | 1400 | 21 | 14.7 | 19 | 1,422 | 100,000 | 42 | 22 | 88 | 92 |
| | | | TOTAL | 84 | 58.8 | NA | NA | 398,000 | NA | NA | NA | NA |
| | | | AVERAGE | NA | NA | 21.7 | 1,330 | 99,500 | 42 | 22 | 60 | 101 |
| 4 | 9/29 | PM | 1600 | 20 | 14 | 19 | 1,373 | 105,000 | 69 | 18 | 24 | 60 |
| 4 | 9/29 | PM | 1800 | 20 | 14 | 22 | 1,369 | 109,000 | 70 | 18 | 28 | 44 |
| 4 | 9/29 | PM | 2000 | 20 | 14 | 23 | 1,241 | 105,000 | 84 | 18 | 24 | 40 |
| 4 | 9/29 | PM | 2200 | 20 | 14 | 27 | 1,251 | 94,000 | 85 | 18 | 16 | 35 |
| | | | TOTAL | 80 | 56 | NA | NA | 413,000 | NA | NA | NA | NA |
| | | | AVERAGE | NA | NA | 22.75 | 1,309 | 103,250 | 77 | 18 | 23 | 45 |

TABLE 4.3 SUMMARY OF FACILITY C OPERATING PARAMETERS

| Unit | Date | Shift | Time | Feed Rate (Buckets) | Feed Rate (tons) | Ram Speed (Units) | Probe Temp. (F) | Combust. Air (in-Hg) | ESP (Kv) | ESP (mA) |
|---|---|---|---|---|---|---|---|---|---|---|
| 2 | 9/28 | PM | 1800 | 9 | 9 | 32 | 1,610 | 0.1 | 23 | 300 |
| 2 | 9/28 | PM | 1900 | 6 | 6 | 28 | 1,350 | 0.1 | 23 | 300 |
| 2 | 9/28 | PM | 2000 | 9 | 9 | 28 | 1,590 | 0.1 | 26 | 350 |
| 2 | 9/28 | PM | 2100 | 9 | 9 | 28 | 1,370 | 0.1 | 27 | 350 |
| 2 | 9/28 | PM | 2200 | 9 | 9 | 22 | 1,300 | 0.1 | 26 | 350 |
| 2 | 9/28 | PM | 2300 | | | 22 | 1,270 | 0.1 | 25 | 390 |
| | | | TOTAL | 42 | 42 | NA | NA | NA | NA | NA |
| | | | AVERAGE | NA | NA | 27 | 1,415 | 0.1 | 25 | 340 |
| 2 | 9/29 | PM | 1600 | 10 | 10 | 22 | 1,450 | 0.1 | 27 | 350 |
| 2 | 9/29 | PM | 1700 | 8 | 8 | 30 | 1,410 | 0.1 | 24 | 350 |
| 2 | 9/29 | PM | 1800 | 7 | 7 | 18 | 1,530 | 0.1 | 25 | 350 |
| 2 | 9/29 | PM | 1900 | 10 | 10 | 36 | | 0.1 | | |
| 2 | 9/29 | PM | 2000 | 10 | 10 | 30 | 1,400 | 0.1 | 23 | 350 |
| 2 | 9/29 | PM | 2100 | | | 28 | 1,540 | 0.1 | | |
| | | | TOTAL | 45 | 45 | NA | NA | NA | NA | NA |
| | | | AVERAGE | NA | NA | 27 | 1,466 | 0.1 | 25 | 350 |
| 2 | 9/30 | AM | 900 | 8 | 8 | NA | 1,465 | 0.113 | 26 | 260 |
| 2 | 9/30 | AM | 1000 | 12 | 12 | NA | 1,400 | 0.104 | 23 | 280 |
| 2 | 9/30 | AM | 1100 | 9 | 9 | NA | 1,420 | 0.1 | 24 | 280 |
| 2 | 9/30 | AM | 1200 | 8 | 8 | NA | 1,500 | 0.112 | 25 | 270 |
| 2 | 9/30 | AM | 1300 | 11 | 11 | NA | 1,605 | 0.102 | 25 | 270 |
| 2 | 9/30 | AM | 1400 | 10 | 10 | NA | 1,640 | 0.1 | 25 | 270 |
| | | | TOTAL | 58 | 58 | NA | NA | NA | NA | NA |
| | | | AVERAGE | NA | NA | NA | 1,505 | 0.1 | 25 | 272 |
| 2 | 9/30 | PM | 1500 | 11 | 11 | 30 | 1,600 | 0.1 | 28 | 35 |
| 2 | 9/30 | PM | 1600 | 11 | 11 | 32 | 1,550 | 0.1 | 25 | 35 |
| 2 | 9/30 | PM | 1700 | 8 | 8 | 36 | 1,500 | 0.1 | 27 | 350 |
| 2 | 9/30 | PM | 1800 | 10 | 10 | 26 | 1,560 | 0.1 | 25 | 350 |
| 2 | 9/30 | PM | 1900 | 10 | 10 | 34 | 1,370 | 0.1 | 24 | 350 |
| 2 | 9/30 | PM | 2000 | | | 32 | 1,420 | 0.1 | 25 | 35 |
| | | | TOTAL | 50 | 50 | NA | NA | NA | NA | NA |
| | | | AVERAGE | NA | NA | 32 | 1,500 | 0.1 | 26 | 193 |

## TABLE 4.4 SUMMARY OF FACILITY D OPERATING PARAMETERS

| Unit | Date | Shift | Time | Feed Rate | | Probe Temp. | | Steam Production | | Combustion Air | | ESP | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Unit 1 (Buckets) | Unit 2 (Buckets) | Unit 1 (F) | Unit 2 (F) | Unit 1 (lb/hr) | Unit 2 (lb/hr) | Unit 1 (Units) | Unit 2 (Units) | Unit 1 (Units) | Unit 2 (Units) |
| 1&2 | 10/3 | AM | 900 | 6 | 8 | 1,400 | 1,425 | 68,000 | 62,000 | 14 | 6 | 79 | 45 |
| 1&2 | 10/3 | AM | 1000 | 15 | 16 | 1,450 | 1,500 | 61,000 | 68,000 | 16 | 8 | 80 | 45 |
| 1&2 | 10/3 | AM | 1100 | 12 | 13 | 1,375 | 1,475 | 64,000 | 63,000 | 17 | 8 | 80 | 45 |
| 1&2 | 10/3 | AM | 1200 | 10 | 13 | 1,375 | 1,400 | 66,000 | 59,000 | 17 | 8 | 80 | 45 |
| 1&2 | 10/3 | AM | 1300 | 15 | 13 | 1,250 | 1,500 | 70,000 | 60,000 | 17 | 8 | 78 | 45 |
| 1&2 | 10/3 | AM | 1400 | 14 | 12 | 1,400 | 1,500 | 40,000 | 54,000 | 17 | 7 | 80 | 45 |
| | | | TOTAL | 72 | 75 | NA | NA | 369,000 | 366,000 | NA | NA | NA | NA |
| | | | AVERAGE | NA | NA | 1,375 | 1,467 | 61,500 | 61,000 | 16 | 8 | 80 | 45 |
| 1&2 | 10/3 | PM | 1600 | 11 | 13 | 1,276 | 1,434 | 52,000 | 60,000 | 14 | 6 | 80 | 45 |
| 1&2 | 10/3 | PM | 1700 | 20 | 18 | 1,349 | 1,440 | 70,000 | 68,000 | 14 | 8 | 80 | 45 |
| 1&2 | 10/3 | PM | 1800 | 20 | 20 | 1,420 | 1,427 | 64,000 | 58,000 | 14 | 8 | 80 | 45 |
| 1&2 | 10/3 | PM | 1900 | | | | | | | | | | |
| 1&2 | 10/3 | PM | 2000 | | | | | | | | | | |
| 1&2 | 10/3 | PM | 2100 | | | | | | | | | | |
| | | | TOTAL | 51 | 51 | NA | NA | 186,000 | 186,000 | NA | NA | NA | NA |
| | | | AVERAGE | NA | NA | 1,348 | 1,434 | 62,000 | 62,000 | 14 | 7 | 80 | 45 |
| 1&2 | 10/4 | AM | 900 | 13 | 12 | 1,500 | 1,500 | 92,000 | 66,000 | 13 | 8 | 75 | 45 |
| 1&2 | 10/4 | AM | 1000 | 11 | 12 | 1,450 | 1,500 | 70,000 | 57,000 | 13 | 8 | 75 | 45 |
| 1&2 | 10/4 | AM | 1100 | 13 | 14 | 1,450 | 1,500 | 72,000 | 60,000 | 13 | 6 | 75 | 45 |
| 1&2 | 10/4 | AM | 1200 | 15 | 15 | 1,500 | 1,500 | 72,000 | 60,000 | 13 | 7 | 75 | 45 |
| 1&2 | 10/4 | AM | 1300 | 12 | 14 | 1,500 | 1,500 | 74,000 | 64,000 | 12 | 7 | 75 | 45 |
| 1&2 | 10/4 | AM | 1400 | 14 | 15 | 1,450 | 1,500 | 68,000 | 58,000 | 13 | 6 | 70 | 45 |
| | | | TOTAL | 78 | 82 | NA | NA | 448,000 | 365,000 | NA | NA | NA | NA |
| | | | AVERAGE | NA | NA | 1,475 | 1,500 | 74,667 | 60,833 | 13 | 7 | 74 | 45 |
| 1&2 | 10/4 | PM | 1600 | 16 | 19 | 1,661 | 1,482 | 89,000 | 68,000 | 12 | 6 | 75 | 45 |
| 1&2 | 10/4 | PM | 1700 | 14 | 16 | 1,557 | 1,485 | 72,000 | 68,000 | 8 | 6 | 75 | 45 |
| 1&2 | 10/4 | PM | 1800 | 14 | 17 | 1,647 | 1,474 | 90,000 | 64,000 | 10 | 7 | 75 | 45 |
| 1&2 | 10/4 | PM | 1900 | 13 | 18 | 1,521 | 1,425 | 82,000 | 62,000 | 12 | 6 | 75 | 45 |
| 1&2 | 10/4 | PM | 2000 | 16 | 19 | 1,525 | 1,452 | 86,000 | 62,000 | 12 | 7 | 75 | 45 |
| 1&2 | 10/4 | PM | 2100 | 15 | 17 | 1,547 | 1,465 | 80,000 | 64,000 | 12 | 6 | 75 | 45 |
| | | | TOTAL | 88 | 106 | NA | NA | 499,000 | 388,000 | NA | NA | NA | NA |
| | | | AVERAGE | NA | NA | 1,576 | 1,464 | 83,167 | 64,667 | 11 | 6 | 75 | 45 |

hopper during the previous hour. The tons were then calculated from the bucket number by using the approximate feed crane capacity. The ram speed is also a relative measure of the feed rate, however, it is a relative measure of the feed rate into the incinerator, rather than into the charging hopper. The charging ram (see Figure 3.1) forces the material from the charging hopper into the combustion chamber. The probe temperature indicates the temperature in the incinerator, but because we are not aware of the exact probe location, it is a relative temperature and should not be directly compared between facilities. The next parameter, steam production rate, indicates the pounds per hour of steam generated at the three energy recovery facilities. The combustion air is a relative measure of the amount of air needed in excess of the stoichiometric requirement for complete combustion. The combustion air can be either overfire, which is forced into the combustion chamber from above the combustion zone, or underfire, which is forced into the combustion chamber through the grates below the combustion zone. Finally, the ESP specifications are relative measures of the power consumption by the ESP. As the level of fly ash particulates in the flue gas increase, the ESP power consumption must increase to maintain an adequate removal efficiency.

## 4.2 Solid Samples

The solid samples collected included: fly ash, combined bottom/fly ash, bottom ash, and landfill perimeter composite (i.e., disposed ash). Each of these samples were analyzed for metals, PCBs, and PCDD/PCDFs, and the results were summarized and evaluated. Sections 4.2.1 through 4.2.3 present the analytical result tables for each parameter summarized by sample matrix and facility and a narrative evaluation of these results.

### 4.2.1 Metals

The solid samples were analyzed for total cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), nickel (Ni), zinc (Zn), arsenic (As), selenium (Se), and mercury (Hg). The results of these analyses are presented in Table 4.5.

A review of the fly ash data in Table 4.5 indicated that the variability between shifts and/or units at any given facility was relatively small without any dominant trends, except that at Facility B, Unit 4 generally had higher metal concentrations than Unit 3. The variability between facilities was relatively large compared to that between shifts and units. In general, Facility B had the highest metal concentration (for 5 out of the 11 metals), while Facility C had the lowest metal concentration (for 6 out of the 11 metals). The predominant metals were iron and zinc, which were followed closely by lead, while the least prevalent metal was selenium.

A review of the metals data for the combined bottom/fly ash and bottom ash showed that the variability between shifts and units was relatively high, although no significant trends were observed. The variability between the facilities was very high with the standard deviation generally exceeding the average metal concentrations. Facility B had the highest concentration of metals (the highest or second highest concentrations for 10 out of 11 metals), while Facility A had the lowest concentration of metals (the lowest or second lowest concentrations for 9 out of the 11 metals). The predominant metals were iron, zinc, lead, and copper. Selenium was again the least prevalent.

The landfill perimeter composite metals data showed that the landfill at Facility C had higher concentrations of metals than the Facility D landfill. This result was anticipated because the bottom/fly ash from Facility C contained greater quantities of metals than that from Facility D. Although there were some exceptions, the landfill composite samples generally contained lower concentrations of each metal than their corresponding bottom/fly ash samples. Again, this was expected because the landfill composite samples had been subjected to weathering, which would leach some of the component metals. It is interesting to note that

# TABLE 4.5 TOTAL METALS DATA FOR SOLID SAMPLES

## FLY ASH

| Facility | Sample Description | Cd mg/kg | Cr mg/kg | Cu mg/kg | Fe mg/kg | Pb mg/kg | Mn mg/kg | Ni mg/kg | Zn mg/kg | As mg/kg | Se mg/kg | Hg mg/kg |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A | Unit 1, 9/26, AM | 193 | 79 | 2380 | 17400 | 5550 | 1010 | 106 | 15700 | 41.9 | <5 | 27 |
| A | Unit 1, 9/26, AM, Dup | 186 | 66 | 2040 | 15000 | 5400 | 1020 | 91 | 14500 | 38.0 | <5 | 23 |
| A | Unit 1, 9/26, PM | 215 | 67 | 1870 | 9730 | 5660 | 1060 | 98 | 15100 | 48.8 | <5 | 35 |
| A | Unit 2, 9/26, AM | 222 | 66 | 1250 | 20200 | 5480 | 807 | 97 | 17400 | 36.8 | <5 | 25 |
| A | Unit 2, 9/26, PM | 138 | 76 | 1040 | 15900 | 6090 | 1090 | 160 | 9480 | 16.0 | <5 | 24 |
| | FACILITY A AVERAGE | 190.8 | 70.8 | 1716 | 15646 | 5636 | 997 | 110 | 14436 | 36.3 | 2.5 | 26.8 |
| | STANDARD DEVIATION | 29.6 | 5.6 | 499 | 3444 | 243 | 99 | 25 | 2660 | 11.0 | 0 | 4.3 |
| B | Unit 3, 9/28, AM | 322 | 105 | 745 | 9900 | 7350 | 895 | 80 | 32700 | 106 | <10 | 9.3 |
| B | Unit 3, 9/28, AM, Dup | 316 | 98 | 724 | 9350 | 7270 | 889 | 76 | 31800 | 89.9 | <10 | 8.0 |
| B | Unit 3, 9/29, PM | 251 | 74 | 588 | 5960 | 5280 | 824 | 52 | 23600 | 79.0 | 10.0 | 12 |
| B | Unit 4, 9/28, AM | 381 | 97 | 912 | 16200 | 9230 | 1310 | 67 | 34000 | 131 | 11.7 | 19 |
| B | Unit 4, 9/29, PM | 475 | 100 | 854 | 22300 | 14400 | 1070 | 68 | 38800 | 149 | 15.6 | 21 |
| | FACILITY B AVERAGE | 349.0 | 94.8 | 765 | 12742 | 8706 | 998 | 69 | 32180 | 111.0 | 9.5 | 13.9 |
| | STANDARD DEVIATION | 75.3 | 10.8 | 112 | 5812 | 3109 | 176 | 10 | 4923 | 25.8 | 4.1 | 5.2 |
| C | Unit 2, 9/28, PM | 107 | 76 | 1050 | 9030 | 3260 | 320 | 130 | 10200 | 29.0 | 4.9 | 1.3 |
| C | Unit 2, 9/29, PM | 191 | 54 | 531 | 8200 | 3490 | 388 | 102 | 10300 | 16.2 | 7.6 | 5 |
| C | Unit 2, 9/29, PM, Dup | 157 | 52 | 556 | 8450 | 3130 | 382 | 95 | 8460 | 17.7 | 6.2 | 4.0 |
| C | Unit 2, 9/30, AM | 223 | 48 | 484 | 16700 | 3420 | 341 | 245 | 10600 | 26.8 | 7.6 | 3.5 |
| C | Unit 2, 9/30, PM | 188 | 49 | 485 | 14400 | 2830 | 353 | 212 | 9940 | 32.2 | 8.8 | 1.4 |
| | FACILITY C AVERAGE | 173.2 | 55.8 | 621 | 11356 | 3226 | 357 | 157 | 9900 | 24.4 | 7.0 | 3.0 |
| | STANDARD DEVIATION | 39.1 | 10.3 | 216 | 3511 | 234 | 25 | 61 | 750 | 6.3 | 1.3 | 1.5 |
| D | Unit 1-2, 10/3, AM | 259 | 77 | 516 | 8320 | 5450 | 857 | 63 | 22100 | 50.7 | 9.6 | 1.8 |
| D | Unit 1-2, 10/3, AM, Dup | 172 | 67 | 518 | 7190 | 4600 | 751 | 55 | 18600 | 54.5 | 9.1 | 2.0 |
| D | Unit 1-2, 10/3, PM | 286 | 93 | 597 | 8790 | 5770 | 1250 | 86 | 23900 | 60.4 | 15.5 | 1.4 |
| D | Unit 1-2, 10/4, AM | 210 | 89 | 486 | 8960 | 4740 | 1410 | 89 | 17600 | 47.2 | 10.7 | 0.94 |
| D | Unit 1-2, 10/4, PM | 206 | 90 | 510 | 9170 | 4430 | 1190 | 86 | 17300 | 43.2 | 9.6 | 1.0 |
| | FACILITY D AVERAGE | 226.6 | 83.2 | 525 | 8486 | 4998 | 1092 | 76 | 19900 | 51.2 | 10.9 | 1.4 |
| | STANDARD DEVIATION | 40.6 | 9.8 | 38 | 706 | 519 | 248 | 14 | 2630 | 5.9 | 2.4 | 0.4 |
| | TOTAL NUMBER | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 |
| | MINIMUM | 107 | 48 | 484 | 5960 | 2830 | 320 | 52 | 8460 | 16 | 2.5 | 0.94 |
| | MAXIMUM | 475 | 105 | 2380 | 22300 | 14400 | 1410 | 245 | 38800 | 149 | 15.6 | 35 |
| | OVERALL AVERAGE | 235 | 76.2 | 907 | 12058 | 5642 | 861 | 103 | 19104 | 55.7 | 7.5 | 11.3 |
| | STANDARD DEVIATION | 85 | 17.2 | 550 | 4611 | 2534 | 335 | 49 | 8901 | 36.4 | 4.0 | 10.7 |

## TABLE 4.5 TOTAL METALS DATA FOR SOLID SAMPLES

### COMBINED BOTTOM AND FLY ASH

| Facility | Sample Description | Cd mg/kg | Cr mg/kg | Cu mg/kg | Fe mg/kg | Pb mg/kg | Mn mg/kg | Ni mg/kg | Zn mg/kg | As mg/kg | Se mg/kg | Hg mg/kg |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A | Unit 1, 9/26, AM | 17 | 25 | 452 | 5130 | 633 | 281 | 21 | 1810 | 6.1 | <0.5 | 6.8 |
| A | Unit 1, 9/26, PM | 13 | 19 | 387 | 6500 | 585 | 331 | 30 | 1480 | 2.9 | <2.5 | 3.9 |
| A | Unit 2, 9/26, AM | 17 | 12 | 369 | 6650 | 2200 | 184 | 22 | 1730 | 7.9 | <5 | 6.9 |
| A | Unit 2, 9/26, AM, Dup | 15 | 16 | 377 | 9140 | 1140 | 251 | 24 | 3050 | 12.2 | <5 | 5.0 |
| A | Unit 2, 9/26, PM | 37 | 12 | 193 | 2100 | 1670 | 188 | 13 | 1980 | 4.7 | <0.5 | 8.7 |
| | FACILITY A AVERAGE | 19.8 | 16.8 | 356 | 5904 | 1246 | 247 | 22.0 | 2010 | 6.8 | 1.4 | 6.3 |
| | STANDARD DEVIATION | 8.7 | 4.9 | 86 | 2300 | 619 | 56 | 5.5 | 544 | 3.2 | 1.0 | 1.7 |
| C | Unit 2, 9/28, PM | 7.8 | 22 | 329 | 5220 | 259 | 110 | 44 | 545 | 4 | 1.4 | 0.51 |
| C | Unit 2, 9/29, PM | 10 | 332 | 5900 | 22300 | 6950 | 339 | 556 | 1520 | 4.7 | <5. | 0.21 |
| C | Unit 2, 9/30, AM | 24 | 19 | 3420 | 5040 | 1700 | 155 | 42 | 1570 | 5.7 | <5. | 0.62 |
| C | Unit 2, 9/30, AM, Dup | 27 | 26 | 608 | 9720 | 1060 | 1810 | 38 | 3250 | 7 | <0.5 | 0.18 |
| C | Unit 2, 9/30, PM | 20 | 37 | 5900 | 16000 | 13200 | 254 | 93 | 2980 | 22.8 | <5. | 0.59 |
| | FACILITY C AVERAGE | 17.8 | 87.2 | 3231 | 11656 | 4634 | 534 | 154.6 | 1973 | 8.8 | 1.8 | 0.4 |
| | STANDARD DEVIATION | 7.6 | 122.6 | 2432 | 6650 | 4884 | 643 | 201.7 | 1005 | 7.1 | 0.9 | 0.2 |
| D | Unit 1-2, 10/3, AM | 45 | 38 | 424 | 24500 | 3410 | 462 | 37 | 2950 | 16.4 | <2.5 | 0.12 |
| D | Unit 1-2, 10/3, PM | 18 | 28 | 1060 | 8000 | 819 | 797 | 25 | 1920 | 4.3 | <1 | 0.16 |
| D | Unit 1-2, 10/4, AM | 17 | 31 | 289 | 8590 | 571 | 3130 | 26 | 2400 | 5.4 | <1 | 0.21 |
| D | Unit 1-2, 10/4, AM, Dup | 18 | 36 | 728 | 95100 | 612 | 640 | 119 | 46000 | 6.1 | <1 | 0.13 |
| D | Unit 1-2, 10/4, PM | 23 | 43 | 524 | 19000 | 688 | 544 | 82 | 2390 | 6.4 | <2.5 | 0.11 |
| | FACILITY D AVERAGE | 24.2 | 35.2 | 605 | 31038 | 1220 | 1115 | 57.8 | 11132 | 7.7 | 0.8 | 0.1 |
| | STANDARD DEVIATION | 10.6 | 5.3 | 269 | 32638 | 1098 | 1014 | 37.0 | 17437 | 4.4 | 0.4 | 0.0 |
| | TOTAL NUMBER | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 15 |
| | MINIMUM | 7.8 | 12 | 193 | 2100 | 259 | 110 | 13 | 545 | 2.9 | 0.25 | 0.11 |
| | MAXIMUM | 45 | 332 | 5900 | 95100 | 13200 | 3130 | 556 | 46000 | 22.8 | 2.5 | 8.7 |
| | OVERALL AVERAGE | 20.6 | 46.4 | 1397 | 16199 | 2366 | 632 | 78.1 | 5038 | 7.77 | 1.327 | 2.276 |
| | STANDARD DEVIATION | 9.5 | 76.9 | 1921 | 22073 | 3324 | 782 | 131.0 | 10971 | 5.21 | 0.910 | 2.980 |

# TABLE 4.5 TOTAL METALS DATA FOR SOLID SAMPLES

## BOTTOM ASH

| Facility | Sample Description | Cd mg/kg | Cr mg/kg | Cu mg/kg | Fe mg/kg | Pb mg/kg | Mn mg/kg | Ni mg/kg | Zn mg/kg | As mg/kg | Se mg/kg | Hg mg/kg |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| B | Unit 3, 9/28, AM | 2.3 | 105 | 10700 | 12000 | 2920 | 1520 | 35 | 1930 | 3.4 | <5. | 0.36 |
| B | Unit 3, 9/29, PM | 1.1 | 24 | 7250 | 27100 | 1380 | 430 | 17 | 914 | 2.2 | <5. | 0.13 |
| B | Unit 4, 9/28, AM | 3.8 | 66 | 792 | 115000 | 2140 | 1010 | 36 | 2350 | 8.9 | <5. | 0.12 |
| B | Unit 4, 9/28, AM, Dup | 3.5 | 78 | 581 | 24100 | 3930 | 938 | 90 | 5760 | 6.9 | <5. | 0.12 |
| B | Unit 4, 9/29, PM | 43 | 33 | 1720 | 17500 | 3630 | 538 | 29 | 12400 | 24.6 | <5. | 0.13 |
| | No. | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| | Min. | 1.1 | 24 | 581 | 12000 | 1380 | 430 | 17 | 914 | 2.2 | 2.5 | 0.12 |
| | Max. | 43 | 105 | 10700 | 115000 | 3930 | 1520 | 90 | 12400 | 24.6 | 2.5 | 0.36 |
| | Avg. | 10.74 | 61.20 | 4209 | 39140 | 2800 | 887 | 41.4 | 4671 | 9.20 | 2.50 | 0.17 |
| | Std. Dev. | 16.16 | 29.67 | 4060 | 38290 | 942 | 387 | 25.2 | 4194 | 8.06 | 0.00 | 0.09 |

## LANDFILL COMPOSITE

| Facility | Sample Description | Cd mg/kg | Cr mg/kg | Cu mg/kg | Fe mg/kg | Pb mg/kg | Mn mg/kg | Ni mg/kg | Zn mg/kg | As mg/kg | Se mg/kg | Hg mg/kg |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C | Perimeter Composite | 8.7 | 85 | 1190 | 60600 | 709 | 572 | 120 | 4740 | 6.0 | <5 | 0.57 |
| D | Perimeter Composite | 30 | 52 | 402 | 19600 | 1210 | 455 | 51 | 2050 | 14.8 | <2.5 | 0.25 |

although the metal concentrations were typically lower in the weathered ash than in freshly generated ash, considerable metal concentrations remain in the weathered ash suggesting that a major portion of the metals in the ash may not be readily mobile to the environment.

Upon comparing the concentrations of metals in the fly ash to those in the combined bottom/fly and bottom ash, some interesting observations arose. First, the variability between shifts, units, and facilities was substantially higher for the combined and bottom ash than it was for the fly ash. In fact, the variability between shifts and units for the bottom/fly and bottom ash was greater than the variability between facilities for the fly ash. This observation was expected because of the heterogeneous nature of the bottom/fly and bottom ash based on the diverse range of particle sizes compared to the more homogeneous nature of the fly ash. This heterogeneity made it extremely difficult to collect representative, comparable samples, as evidenced by the standard deviations. Second, the concentrations of cadmium, mercury, chromium, lead, nickel, zinc, selenium, and arsenic were between 1.5 and ten times higher in the fly ash than in the bottom/fly or bottom ash. Third, the concentrations of copper and iron are approximately two times higher in the bottom/fly and bottom ash than they are in the fly ash. Finally, the concentration of manganese is approximately equivalent for both ash fractions.

### 4.2.2 Polychlorinated Biphenyls (PCBs)

The solid samples were analyzed for individual PCB homologs and total PCBs. The results of these analyses are tabulated and summarized in Table 4.6.

A review of the PCB homolog concentrations in the fly ash showed that the variability between shifts and units was relatively small, while the variability between facilities was relatively large. Facility D had the highest concentration of total PCBs, as well as the highest concentration of each individual PCB homolog, followed by Facility B,

## TABLE 4.6 PCBs IN SOLID SAMPLES

### FLY ASH

| Plant | Sample Description | MONO -CB ng/g | DI -CB ng/g | TRI -CB ng/g | TETRA -CB ng/g | PENTA -CB ng/g | TOTAL PCB ng/g |
|---|---|---|---|---|---|---|---|
| A | Unit 1, 9/26, AM | | 0.7 | | | | 0.7 |
| A | Unit 1, 9/26, AM, Dup | | 0.73 | | | | 0.73 |
| A | Unit 1, 9/26, PM | | 1.37 | 0.52 | | | 1.89 |
| A | Unit 2, 9/26, AM | 0.64 | 0.13 | | | | 0.77 |
| A | Unit 2, 9/26, PM | | | | | | 0 |
| | FACILITY A AVERAGE | 0.64 | 0.73 | 0.52 | | | 0.82 |
| | STANDARD DEVIATION | 0.00 | 0.44 | 0.00 | | | 0.61 |
| B | Unit 3, 9/28, AM | | | | | | 0 |
| B | Unit 3, 9/28, AM, Dup | | | | | | 0 |
| B | Unit 3, 9/29, PM | 0.5 | 2.01 | 2.82 | 2.72 | 0.87 | 8.92 |
| B | Unit 4, 9/28, AM | | | 1.34 | 2.5 | | 3.84 |
| B | Unit 4, 9/29, PM | 0.29 | 0.38 | 2.43 | 2.45 | | 5.55 |
| | FACILITY B AVERAGE | 0.40 | 1.19 | 2.20 | 2.56 | 0.87 | 3.66 |
| | STANDARD DEVIATION | 0.10 | 0.82 | 0.63 | 0.12 | 0.00 | 3.41 |
| C | Unit 2, 9/28, PM | | | | | | 0 |
| C | Unit 2, 9/29, PM | | | | | | 0 |
| C | Unit 2, 9/29, PM, Dup | | 0.81 | | | | 0.81 |
| C | Unit 2, 9/30, AM | | | | | | 0 |
| C | Unit 2, 9/30, PM | | 0.49 | | | | 0.49 |
| C | Unit 2, Coarse | | | | | | 0 |
| C | Unit 2, Fine (ESP) | | | | | | 0 |
| C | Unit 2, Medium | | | | | | 0 |
| | FACILITY C AVERAGE | | 0.65 | | | | 0.16 |
| | STANDARD DEVIATION | | 0.16 | | | | 0.29 |
| D | Unit 1-2, 10/3, AM | | 2.88 | 2.91 | 2.41 | | 8.2 |
| D | Unit 1-2, 10/3, AM, Dup | | 2.42 | 1.72 | 1.02 | | 5.16 |
| D | Unit 1-2, 10/3, PM | 0.88 | 5 | 5.27 | 2.16 | | 13.31 |
| D | Unit 1-2, 10/4, AM | 1.46 | 7.87 | 7.67 | 5.52 | 2.25 | 24.77 |
| D | Unit 1-2, 10/4, PM | 0.47 | 1.84 | 1.98 | 1.31 | | 5.6 |
| | FACILITY D AVERAGE | 0.94 | 4.00 | 3.91 | 2.48 | 2.25 | 11.41 |
| | STANDARD DEVIATION | 0.41 | 2.21 | 2.26 | 1.60 | 0.00 | 7.28 |
| | TOTAL NUMBER | 6 | 13 | 9 | 8 | 2 | 20 |
| | MINIMUM | 0.29 | 0.13 | 0.52 | 1.02 | 0.87 | 0 |
| | MAXIMUM | 1.46 | 7.87 | 7.67 | 5.52 | 2.25 | 24.77 |
| | OVERALL AVERAGE | 0.707 | 2.048 | 2.962 | 2.511 | 1.560 | 4.037 |
| | STANDARD DEVIATION | 0.382 | 2.111 | 2.079 | 1.270 | 0.690 | 6.005 |

# TABLE 4.6 PCBs IN SOLID SAMPLES

## COMBINED BOTTOM AND FLY ASH

| Plant | Sample Description | MONO -CB ng/g | DI -CB ng/g | TRI -CB ng/g | TETRA -CB ng/g | PENTA -CB ng/g | TOTAL PCB ng/g |
|---|---|---|---|---|---|---|---|
| A | Unit 1, 9/26, AM | | | | | | 0 |
| A | Unit 1, 9/26, PM | | 0.66 | | | | 0.66 |
| A | Unit 2, 9/26, AM | | | | | | 0 |
| A | Unit 2, 9/26, AM, Dup | | | | | | 0 |
| A | Unit 2, 9/26, PM | | | | | | 0 |
| | NUMBER OF PCBs FOUND | 0 | 1 | 0 | 0 | 0 | 1 |
| C | Unit 2, 9/28, PM | | | | | | 0 |
| C | Unit 2, 9/29, PM | | | | | | 0 |
| C | Unit 2, 9/30, AM | | | | | | 0 |
| C | Unit 2, 9/30, AM, Dup | | | | | | 0 |
| C | Unit 2, 9/30, PM | | | | | | 0 |
| | NUMBER OF PCBs FOUND | 0 | 0 | 0 | 0 | 0 | 0 |
| D | Unit 1-2, 10/3, AM | | | 0.35 | | | 0.35 |
| D | Unit 1-2, 10/3, PM | | | 5.66 | | | 5.66 |
| D | Unit 1-2, 10/4, AM | | | 2.79 | | | 2.79 |
| D | Unit 1-2, 10/4, AM, Dup | | 1.35 | 14.3 | 16.5 | | 32.15 |
| D | Unit 1-2, 10/4, PM | | 0.126 | 9.52 | | | 9.646 |
| | NUMBER OF PCBs FOUND | 0 | 2 | 5 | 1 | 0 | 8 |
| | TOTAL NUMBER | 0 | 3 | 5 | 1 | 0 | 15 |
| | MINIMUM | NA | 0.126 | 0.35 | 16.5 | NA | 0 |
| | MAXIMUM | NA | 1.35 | 14.3 | 16.5 | NA | 32.15 |
| | OVERALL AVERAGE | NA | 0.71 | 6.52 | 16.50 | NA | 3.42 |
| | STANDARD DEVIATION | NA | 0.50 | 4.94 | 0.00 | NA | 8.13 |

## TABLE 4.6 PCBs IN SOLID SAMPLES

### BOTTOM ASH

| Plant | Sample Description | MONO -CB ng/g | DI -CB ng/g | TRI -CB ng/g | TETRA -CB ng/g | PENTA -CB ng/g | TOTAL PCB ng/g |
|---|---|---|---|---|---|---|---|
| B | Unit 3, 9/28, AM | | | | | | 0 |
| B | Unit 3, 9/29, PM | | | | | | 0 |
| B | Unit 4, 9/28, AM | | | | | | 0 |
| B | Unit 4, 9/28, AM, Dup | | | | | | 0 |
| B | Unit 4, 9/29, PM | | | | | | 0 |
| | NUMBER OF PCBs FOUND | 0 | 0 | 0 | 0 | 0 | 0 |

### LANDFILL COMPOSITE

| Plant | Sample Description | MONO -CB ng/g | DI -CB ng/g | TRI -CB ng/g | TETRA -CB ng/g | PENTA -CB ng/g | TOTAL PCB ng/g |
|---|---|---|---|---|---|---|---|
| C | Perimeter Composite | | 41.5 | 225 | 109 | | 375.5 |
| D | Perimeter Composite | | 0.689 | 2.36 | 1.54 | | 4.589 |

Facility A, and Facility C, which had the lowest concentration of each PCB homolog. The di-, tri-, and tetra-CB homologs were the most prevalent and were of approximately equal magnitude, while the mono- and Penta-CB homologs were also approximately equal, but substantially less prevalent than the di-, tri-, and tetra-CB homologs. The higher chlorinated PCB homologs (i.e., the PCB homologs more highly chlorinated than the Penta-CB class) were not detected in any fly ash sample.

A review of the PCB data in Table 4.6 for the combined bottom/fly ash and bottom ash (Facility B) showed that only Facility D had measurable concentrations of PCBs in each sample. Therefore, the variability between facilities was significantly high. Only one sample from Facility A (Unit 1, 9/26, PM) had a detectable, although minimal, PCB concentration of 0.66 ng/g. Facilities B and C did not have any samples in which PCBs were detected. As was the case for the fly ash, the di-, tri-, and tetra-CB homologs were the most prevalent. In fact, these were the only PCB homologs detected in any of the combined ash samples. The tri-CB homolog was detected in all five samples from Facility D, while the tetra-CB homolog was detected in only one sample from Facility D. The di-CB homolog was detected in two samples from Facility D and in one sample from Facility A.

The landfill perimeter composite samples also contained only the di-, tri-, and tetra-CB homologs. The PCB concentration of the landfill composite from Facility D was approximately equal to the PCB concentration in the combined ash samples from Facility D, as expected. However, the PCB concentration for the landfill composite from Facility C was the highest found in any sample (375.5 ng/g), yet the combined ash samples from this facility did not contain any detectable PCBs. It was anticipated that the results from Facility C would have exhibited the same trend noted for Facility D; however, several different contributing factors may have caused this seemingly erroneous result from Facility C. First, an organic interference (see discussion of analytical procedures in Section 3.4.2) in the landfill composite sample may have caused an erroneously high PCB result for this sample. Second, because of the heterogeneous nature of the disposed ash, some "pockets" of concentrated ash may have been sampled and subsequently biased the composite. Third, an outside source of PCBs may have contaminated the ash once the residue had been placed in the disposal area. One potential outside source of PCBs was the bulldozer or other diesel powered equipment used at the landfill. Typically, this equipment uses hydraulic fluids that may contain PCBs. If these hydraulic fluids were leaking, they may have contributed to the high concentration of PCBs in the landfill perimeter composite, especially since the bulldozer operates principally around the landfill's perimeter.

Upon comparing the PCB concentrations of the fly ash with those of the combined and bottom ash, the following observations were noted. First, the variability between shifts, units, and facilities for the combined/bottom ash was substantially higher (i.e., where measurable quantities were detected) than for the fly ash. This is due to the heterogeneity of the combined/bottom ash compared to the homogeneity of the fly ash. Second, the PCB concentrations of the fly ash were significantly higher than those for the combined/bottom ash. This indicates that the PCBs may condense on the fine fly ash particles or physically adhere to them and are negligible in the coarse bottom ash material. Third, only the di-, tri-, and tetra-CB homologs were detected in both the fly ash and combined ash, and the mono- and penta-CB homologs were found only in the fly ash. This indicates that the bottom ash alone is not a source of mono- or penta-CB homologs, and it dilutes the concentration of these homologs below detectability in the combined ash. This observation is supported by the bottom ash data for Facility B. Finally, Facility D had the highest concentrations of PCBs for both the fly ash and combined ash, and Facility C had the lowest PCB concentrations for both ash fractions.

### 4.2.3 Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzo-furans (PCDD/PCDFs)

The solid samples were analyzed for individual PCDD and PCDF homologs in the tetra- through octa-chlorinated classes. Additionally, the 2,3,7,8-TCDD and 2,3,7,8-TCDF isomers were identified and quantified. The results of these analyses are tabulated and summarized by sample matrix and facility in Table 4.7.

A review of the PCDD homolog concentrations in the fly ash showed that the variability of the homolog concentrations between units and shifts was relatively small, and the variability of these concentrations between facilities was extremely large. Facility C had the highest concentration of total PCDDs, as well as the highest concentration of each PCDD homolog. Additionally, Facility C had the highest concentration of the 2,3,7,8-TCDD isomer. After Facility C, Facility B had the second highest concentration of each PCDD homolog, followed by Facility D and Facility A, which had the lowest concentration of each PCDD homolog. The hexa-CDD homolog was the most prevalent at three of the four facilities (it was the third most prevalent at Facility B), and the tetra-CDD homolog was the least prevalent at all four facilities. Approximately 5 percent of the total tetra-CDDs was the 2,3,7,8-TCDD isomer. Finally, one significant trend was noted, as the total PCDDs increased, the hexa- through octa-chlorinated classes abundance increased disproportionately (i.e., when the total PCDD concentration was less than 500 ng/g, the hexa- through octa-chlorinated classes accounted for 70 percent of the total PCDD concentration, however, when the total PCDD concentrations exceeded 500 ng/g, the hexa- through octa-chlorinated classes accounted for 90 percent of the total PCDD concentration).

At Facility C, two discrete fly ash fractions were also analyzed for PCDDs. The first of these, the coarse fly ash (i.e., economizer ash), did not contain any detectable PCDDs. However, the second of these fractions, the fine fly ash (i.e., electrostatic precipitator ash), contained the highest PCDD concentrations of any fly ash sample that was

## TABLE 4.7 PCDD AND PCDF IN SOLID SAMPLES

### FLY ASH (DIOXIN HOMOLOGS)

| Plant | Sample Description | 2,3,7,8 TCDD (ng/g) | TETRA -CDD (ng/g) | PENTA -CDD (ng/g) | HEXA -CDD (ng/g) | HEPTA -CDD (ng/g) | OCTA -CDD (ng/g) | TOTAL -CDD (ng/g) |
|---|---|---|---|---|---|---|---|---|
| A | Unit 1, 9/26, AM | 0.093 | 2.3 | 11 | 20 | 14 | 17 | 64.3 |
| A | Unit 1, 9/26, AM, Dup | 0.11 | 2.8 | 14 | 20 | 14 | 18 | 68.8 |
| A | Unit 1, 9/26, PM | 0.13 | 4.7 | 20 | 35 | 26 | 31 | 116.7 |
| A | Unit 2, 9/26, AM | 0.24 | 5.2 | 16 | 18 | 14 | 13 | 66.2 |
| A | Unit 2, 9/26, PM | 0.22 | 6.6 | 32 | 24 | 14 | 11 | 87.6 |
| | FACILITY A AVERAGE | 0.16 | 4.32 | 18.60 | 23.40 | 16.40 | 18.00 | 80.7 |
| | STANDARD DEVIATION | 0.06 | 1.58 | 7.31 | 6.12 | 4.80 | 6.99 | 19.8 |
| B | Unit 3, 9/28, AM | 0.38 | 12 | 139 | 126 | 100 | 96 | 473 |
| B | Unit 3, 9/28, AM, Dup | 0.38 | 11 | 114 | 123 | 93 | 89 | 430 |
| B | Unit 3, 9/29, PM | 0.63 | 18 | 137 | 322 | 203 | 210 | 890 |
| B | Unit 4, 9/28, AM | 0.24 | 6.5 | 84 | 207 | 352 | 586 | 1235.5 |
| B | Unit 4, 9/29, PM | 0.13 | 7.0 | 99 | 209 | 435 | 1363 | 2113 |
| | FACILITY B AVERAGE | 0.35 | 10.90 | 114.60 | 197 | 237 | 469 | 1028 |
| | STANDARD DEVIATION | 0.17 | 4.15 | 21.34 | 73 | 136 | 482 | 617 |
| C | Unit 2, 9/28, PM | 2.2 | 27 | 238 | 697 | 331 | 393 | 1686 |
| C | Unit 2, 9/29, PM | 1.5 | 31 | 710 | 5565 | 1759 | 2460 | 10525 |
| C | Unit 2, 9/29, PM, Dup | 2.1 | 33 | 722 | 3946 | 3030 | 3152 | 10883 |
| C | Unit 2, 9/30, AM | 2.4 | 43 | 513 | 1430 | 1751 | 2338 | 6075 |
| C | Unit 2, 9/30, PM | 1.5 | 18 | 335 | 1052 | 1089 | 1433 | 3927 |
| C | Unit 2, Coarse | <0.14 | <0.14 | <0.02 | <0.03 | <0.06 | <0.16 | 0 |
| C | Unit 2, Fine (ESP) | 3.9 | 38 | 980 | 3400 | 4900 | 2700 | 12018 |
| | FACILTIY C AVERAGE | 1.95 | 27.2 | 500 | 2299 | 1837 | 1782 | 6445 |
| | STANDARD DEVIATION | 1.07 | 13.3 | 309 | 1880 | 1559 | 1116 | 4441 |
| D | Unit 1-2, 10/3, AM | 0.38 | 5.2 | 54 | 105 | 45 | 44 | 253.2 |
| D | Unit 1-2, 10/3, AM, Dup | 0.45 | 5.1 | 46 | 103 | 48 | 48 | 250.1 |
| D | Unit 1-2, 10/3, PM | 0.83 | 19 | 91 | 106 | 81 | 113 | 410 |
| D | Unit 1-2, 10/4, AM | 0.66 | 11 | 61 | 89 | 39 | 35 | 235 |
| D | Unit 1-2, 10/4, PM | 0.37 | 7.9 | 45 | 49 | 37 | 37 | 175.9 |
| | FACILITY D AVERAGE | 0.54 | 9.64 | 59.4 | 90.4 | 50.0 | 55.4 | 265 |
| | STANDARD DEVIATION | 0.18 | 5.15 | 16.8 | 21.6 | 16.0 | 29.2 | 77.7 |
| | TOTAL NUMBER | 22 | 22 | 22 | 22 | 22 | 22 | 22 |
| | MINIMUM | 0.07 | 0.07 | 0.01 | 0.015 | 0.03 | 0.08 | 0 |
| | MAXIMUM | 3.9 | 43 | 980 | 5565 | 4900 | 3152 | 12018 |
| | OVERALL AVERAGE | 0.86 | 14.3 | 203 | 802 | 653 | 690 | 2363 |
| | STANDARD DEVIATION | 0.98 | 12.2 | 270 | 1475 | 1199 | 1017 | 3775 |

## TABLE 4.7 PCDD AND PCDF IN SOLID SAMPLES

### FLY ASH (FURAN HOMOLOGS)

| Plant | Sample Description | 2,3,7,8 TCDF (ng/g) | TETRA -CDF (ng/g) | PENTA -CDF (ng/g) | HEXA -CDF (ng/g) | HEPTA -CDF (ng/g) | OCTA -CDF (ng/g) | TOTAL -CDF (ng/g) | TCDD + TCDF (ng/g) |
|---|---|---|---|---|---|---|---|---|---|
| A | Unit 1, 9/26, AM | | 20 | 7.1 | 17 | 14 | 2.1 | 60.2 | 124.5 |
| A | Unit 1, 9/26, AM, Dup | | 23 | 10 | 14 | 12 | 2.3 | 61.3 | 130.1 |
| A | Unit 1, 9/26, PM | | 34 | 15 | 23 | 22 | 4.0 | 98 | 214.7 |
| A | Unit 2, 9/26, AM | | 52 | 16 | 96 | 44 | 1.4 | 209.4 | 275.6 |
| A | Unit 2, 9/26, PM | | 89 | 32 | 18 | 9.9 | 2.0 | 150.9 | 238.5 |
| | FACILITY A AVERAGE | | 43.6 | 16.0 | 33.6 | 20.4 | 2.4 | 116.0 | 196.7 |
| | STANDARD DEVIATION | | 25.3 | 8.6 | 31.3 | 12.5 | 0.9 | 57.2 | 59.9 |
| B | Unit 3, 9/28, AM | | 91 | 64 | 56 | 40 | 8.1 | 259.1 | 732.1 |
| B | Unit 3, 9/28, AM, Dup | | 97 | 65 | 61 | 40 | 8.3 | 271.3 | 701.3 |
| B | Unit 3, 9/29, PM | | 107 | 61 | 241 | 19 | 21 | 449 | 1339 |
| B | Unit 4, 9/28, AM | | 48 | 37 | 41 | 49 | 11 | 186 | 1421.5 |
| B | Unit 4, 9/29, PM | | 59 | 46 | 54 | 63 | 34 | 256 | 2369 |
| | FACILITY B AVERAGE | | 80.4 | 54.6 | 90.6 | 42.2 | 16.5 | 284 | 1313 |
| | STANDARD DEVIATION | | 22.8 | 11.1 | 75.5 | 14.3 | 9.9 | 87.6 | 606 |
| C | Unit 2, 9/28, PM | | 61 | 56 | 54 | 10 | 24 | 205 | 1891 |
| C | Unit 2, 9/29, PM | | 164 | 221 | 336 | 32 | 60 | 813 | 11338 |
| C | Unit 2, 9/29, PM, Dup | | 169 | 226 | 2353 | 77 | 362 | 3187 | 14070 |
| C | Unit 2, 9/30, AM | | 130 | 153 | 473 | 666 | 108 | 1530 | 7605 |
| C | Unit 2, 9/30, PM | | 73 | 93 | 638 | 610 | 175 | 1589 | 5516 |
| C | Unit 2, Coarse | 0.66 | 3.8 | 1.5 | 0.22 | <0.03 | <0.15 | 5.52 | 5.52 |
| C | Unit 2, Fine (ESP) | 26 | 110 | 310 | 590 | 570 | 170 | 1750 | 13768 |
| | FACILITY C AVERAGE | 13 | 102 | 152 | 635 | 281 | 128 | 1297 | 7742 |
| | STANDARD DEVIATION | 13 | 55 | 100 | 738 | 292 | 114 | 1001 | 5187 |
| D | Unit 1-2, 10/3, AM | | 36 | 32 | 115 | 80 | 4.9 | 267.9 | 521.1 |
| D | Unit 1-2, 10/3, AM, Dup | | 36 | 27 | 21 | 3.8 | 5.6 | 93.4 | 343.5 |
| D | Unit 1-2, 10/3, PM | | 93 | 47 | 87 | 75 | 9.8 | 311.8 | 721.8 |
| D | Unit 1-2, 10/4, AM | | 70 | 32 | 87 | 50 | 3.1 | 242.1 | 477.1 |
| D | Unit 1-2, 10/4, PM | | 53 | 27 | 37 | 29 | 3.7 | 149.7 | 325.6 |
| | FACILITY D AVERAGE | | 57.6 | 33.0 | 69.4 | 47.6 | 5.4 | 213 | 478 |
| | STANDARD DEVIATION | | 21.7 | 7.3 | 34.9 | 28.5 | 2.4 | 79.9 | 143 |
| | TOTAL NUMBER | 2 | 22 | 22 | 22 | 22 | 22 | 22 | 22 |
| | MINIMUM | 0.66 | 3.8 | 1.5 | 0.22 | 0.015 | 0.075 | 5.52 | 5.52 |
| | MAXIMUM | 26 | 169 | 310 | 2353 | 666 | 362 | 3187 | 14070 |
| | OVERALL AVERAGE | 13.33 | 73.6 | 71.8 | 246 | 114 | 46 | 552 | 2915 |
| | STANDARD DEVIATION | 12.67 | 43.2 | 80.0 | 496 | 201 | 86 | 765 | 4436 |

## TABLE 4.7 PCDD AND PCDF IN SOLID SAMPLES

### COMBINED BOTTOM ASH AND FLY ASH (DIOXIN HOMOLOGS)

| Plant | Sample Description | 2,3,7,8 TCDD (ng/g) | TETRA -CDD (ng/g) | PENTA -CDD (ng/g) | HEXA -CDD (ng/g) | HEPTA -CDD (ng/g) | OCTA -CDD (ng/g) | TOTAL -CDD (ng/g) |
|---|---|---|---|---|---|---|---|---|
| A | Unit 1, 9/26, AM | 0.02 | 1.5 | 2.7 | 1.9 | 1.7 | 0.89 | 8.69 |
| A | Unit 1, 9/26, PM | | | | | | | |
| A | Unit 2, 9/26, AM | 0.07 | 2.2 | 3.2 | 2 | 1.5 | 0.84 | 9.74 |
| A | Unit 2, 9/26, PM | 0.33 | 13 | 19 | 11 | 8.2 | 3.7 | 54.9 |
| | FACILITY A AVERAGE | 0.14 | 5.57 | 8.30 | 4.97 | 3.80 | 1.81 | 24.44 |
| | STANDARD DEVIATION | 0.14 | 5.26 | 7.57 | 4.27 | 3.11 | 1.34 | 21.54 |
| C | Unit 2, 9/28, PM | 0.12 | 2.2 | 11 | 13 | 15 | 7.7 | 48.9 |
| C | Unit 2, 9/29, PM | 0.13 | 2 | 11 | 18 | 31 | 18 | 80 |
| C | Unit 2, 9/30, AM | 0.62 | 14 | 47 | 67 | 120 | 89 | 337 |
| C | Unit 2, 9/30, AM, Dup | 0.78 | 13 | 50 | 78 | 120 | 89 | 350 |
| C | Unit 2, 9/30, PM | <0.31 | 1.3 | 10 | 11 | 22 | 18 | 62.3 |
| | FACILITY C AVERAGE | 0.36 | 6.50 | 25.8 | 37.4 | 61.6 | 44.3 | 176 |
| | STANDARD DEVIATION | 0.28 | 5.73 | 18.6 | 29.0 | 48.0 | 36.7 | 137 |
| D | Unit 1-2, 10/3, AM | 0.07 | 1.3 | 4 | 3.4 | 3.3 | 2.6 | 14.6 |
| D | Unit 1-2, 10/3, PM | <0.08 | 0.46 | 2.3 | 1.4 | 1.4 | 1.4 | 6.96 |
| D | Unit 1-2, 10/4, AM | <0.28 | <0.28 | 1.9 | 1.5 | 1.5 | 1.3 | 6.2 |
| D | Unit 1-2, 10/4, PM | 0.04 | 1.1 | 2.6 | 1.8 | 1.6 | 1.2 | 8.3 |
| | FACILITY D AVERAGE | 0.07 | 0.75 | 2.70 | 2.03 | 1.95 | 1.63 | 9.02 |
| | STANDARD DEVIATION | 0.04 | 0.47 | 0.79 | 0.81 | 0.78 | 0.57 | 3.31 |
| | TOTAL NUMBER | 12 | 12 | 12 | 12 | 12 | 12 | 12 |
| | MINIMUM | 0.02 | 0.14 | 1.9 | 1.4 | 1.4 | 0.84 | 6.2 |
| | MAXIMUM | 0.78 | 14 | 50 | 78 | 120 | 89 | 350 |
| | OVERALL AVERAGE | 0.21 | 4.35 | 13.7 | 17.5 | 27.3 | 19.5 | 82.3 |
| | STANDARD DEVIATION | 0.24 | 5.23 | 16.3 | 25.3 | 42.5 | 31.7 | 119 |

## TABLE 4.7 PCDD AND PCDF IN SOLID SAMPLES

### COMBINED BOTTOM ASH AND FLY ASH (FURAN HOMOLOGS)

| Plant | Sample Description | 2,3,7,8 TCDF (ng/g) | TETRA -CDF (ng/g) | PENTA -CDF (ng/g) | HEXA -CDF (ng/g) | HEPTA -CDF (ng/g) | OCTA -CDF (ng/g) | TOTAL -CDF (ng/g) | TCDD + TCDF (ng/g) |
|---|---|---|---|---|---|---|---|---|---|
| A | Unit 1, 9/26, AM | 0.88 | 6.3 | 2.5 | 1.3 | 0.62 | 0.18 | 10.9 | 19.59 |
| A | Unit 1, 9/26, PM | | | | | | | | |
| A | Unit 2, 9/26, AM | 2.4 | 20 | 6.7 | 3.2 | 1.2 | 0.28 | 31.38 | 41.12 |
| A | Unit 2, 9/26, PM | 12 | 91 | 37 | 18 | 6.6 | 1.3 | 153.9 | 208.8 |
| | FACILITY A AVERAGE | 5.09 | 39.10 | 15.40 | 7.50 | 2.81 | 0.59 | 65.4 | 89.8 |
| | STANDARD DEVIATION | 4.92 | 37.12 | 15.37 | 7.47 | 2.69 | 0.51 | 63.1 | 84.6 |
| C | Unit 2, 9/28, PM | 0.8 | 5 | 5.2 | 6.4 | 4.8 | 1.4 | 22.8 | 71.7 |
| C | Unit 2, 9/29, PM | 0.89 | 4.7 | 5.5 | 11 | 8 | 1.8 | 31 | 111 |
| C | Unit 2, 9/30, AM | 2.9 | 20 | 20 | 24 | 27 | 6.7 | 97.7 | 434.7 |
| C | Unit 2, 9/30, AM, Dup | 3.8 | 24 | 27 | 35 | 36 | 8.4 | 130.4 | 480.4 |
| C | Unit 2, 9/30, PM | 0.55 | 3.4 | 4.8 | 6.3 | 8.2 | 2.1 | 24.8 | 87.1 |
| | FACILITY C AVERAGE | 1.79 | 11.42 | 12.50 | 16.54 | 16.80 | 4.08 | 61.34 | 237 |
| | STANDARD DEVIATION | 1.31 | 8.75 | 9.25 | 11.27 | 12.39 | 2.89 | 44.34 | 181 |
| D | Unit 1-2, 10/3, AM | 0.76 | 5.1 | 4.7 | 4.1 | 2.6 | 0.59 | 17.09 | 31.69 |
| D | Unit 1-2, 10/3, PM | 0.44 | 3.1 | 2 | 1.3 | 0.81 | 0.27 | 7.48 | 14.44 |
| D | Unit 1-2, 10/4, AM | 0.41 | 2.3 | 1.6 | 1.2 | 0.83 | 0.21 | 6.14 | 12.34 |
| D | Unit 1-2, 10/4, PM | 0.62 | 3.4 | 2.2 | 1.8 | 1.1 | 0.23 | 8.73 | 17.03 |
| | FACILITY D AVERAGE | 0.56 | 3.48 | 2.63 | 2.10 | 1.34 | 0.33 | 9.86 | 18.88 |
| | STANDARD DEVIATION | 0.14 | 1.02 | 1.22 | 1.18 | 0.74 | 0.15 | 4.27 | 7.58 |
| | TOTAL NUMBER | 12 | 12 | 12 | 12 | 12 | 12 | 12 | 12 |
| | MINIMUM | 0.41 | 2.3 | 1.6 | 1.2 | 0.62 | 0.18 | 6.14 | 12.34 |
| | MAXIMUM | 12 | 91 | 37 | 35 | 36 | 8.4 | 153.9 | 480.4 |
| | OVERALL AVERAGE | 2.20 | 15.69 | 9.93 | 9.47 | 8.15 | 1.96 | 45.2 | 127 |
| | STANDARD DEVIATION | 3.14 | 23.90 | 11.10 | 10.35 | 10.95 | 2.61 | 49.5 | 157 |

## TABLE 4.7 PCDD AND PCDF IN SOLID SAMPLES

### BOTTOM ASH (DIOXIN HOMOLOGS)

| Plant | Sample Description | 2,3,7,8 TCDD (ng/g) | TETRA -CDD (ng/g) | PENTA -CDD (ng/g) | HEXA -CDD (ng/g) | HEPTA -CDD (ng/g) | OCTA -CDD (ng/g) | TOTAL -CDD (ng/g) |
|---|---|---|---|---|---|---|---|---|
| B | Unit 3, 9/28, AM | <0.04 | <0.04 | <0.01 | 0.02 | 0.09 | 0.16 | 0.27 |
| B | Unit 3, 9/29, PM | <0.04 | <0.04 | <0.02 | 0.03 | 0.13 | 0.16 | 0.32 |
| B | Unit 4, 9/28, AM | <0.08 | <0.08 | <0.05 | 0.07 | 0.13 | 0.35 | 0.55 |
| B | Unit 4, 9/28, AM, Dup | 0.01 | 0.11 | 0.21 | 0.16 | 0.24 | 0.61 | 1.33 |
| B | Unit 4, 9/29, PM | <0.14 | 0.65 | 2 | 2.3 | 6.3 | 29 | 40.25 |
| | FACILITY B AVERAGE | 0.03 | 0.17 | 0.45 | 0.52 | 1.38 | 6.06 | 8.54 |
| | STANDARD DEVIATION | 0.02 | 0.24 | 0.78 | 0.89 | 2.46 | 11.47 | 15.86 |

### BOTTOM ASH (FURAN HOMOLOGS)

| Plant | Sample Description | 2,3,7,8 TCDF (ng/g) | TETRA -CDF (ng/g) | PENTA -CDF (ng/g) | HEXA -CDF (ng/g) | HEPTA -CDF (ng/g) | OCTA -CDF (ng/g) | TOTAL -CDF (ng/g) | TCDD + TCDF (ng/g) |
|---|---|---|---|---|---|---|---|---|---|
| B | Unit 3, 9/28, AM | 0.03 | 0.15 | 0.07 | 0.02 | 0.04 | <0.04 | 0.28 | 0.55 |
| B | Unit 3, 9/29, PM | 0.02 | 0.06 | 0.02 | 0.05 | 0.03 | <0.04 | 0.16 | 0.48 |
| B | Unit 4, 9/28, AM | 0.05 | 0.28 | 0.18 | 0.1 | 0.1 | 0.06 | 0.72 | 1.27 |
| B | Unit 4, 9/28, AM, Dup | 0.09 | 0.68 | 0.33 | 0.26 | 0.26 | 0.12 | 1.65 | 2.98 |
| B | Unit 4, 9/29, PM | 0.3 | 1.3 | 1.5 | 2.5 | 6.9 | 3.7 | 15.9 | 56.15 |
| | FACILITY B AVERAGE | 0.10 | 0.49 | 0.42 | 0.59 | 1.47 | 0.78 | 3.74 | 12.29 |
| | STANDARD DEVIATION | 0.10 | 0.46 | 0.55 | 0.96 | 2.72 | 1.46 | 6.10 | 21.95 |

## TABLE 4.7 PCDD AND PCDF IN SOLID SAMPLES

### LANDFILL COMPOSITE (DIOXIN HOMOLOGS)

| Plant | Sample Description | 2,3,7,8 TCDD (ng/g) | TETRA -CDD (ng/g) | PENTA -CDD (ng/g) | HEXA -CDD (ng/g) | HEPTA -CDD (ng/g) | OCTA -CDD (ng/g) | TOTAL -CDD (ng/g) |
|---|---|---|---|---|---|---|---|---|
| C | Perimeter Composite | 0.07 | 1.2 | 5.7 | 6.8 | 9 | 6.1 | 28.8 |
| D | Perimeter Composite | 0.15 | 2.5 | 6 | 4.1 | 4.2 | 3.9 | 20.7 |

### LANDFILL COMPOSITE (FURAN HOMOLOGS)

| Plant | Sample Description | 2,3,7,8 TCDF (ng/g) | TETRA -CDF (ng/g) | PENTA -CDF (ng/g) | HEXA -CDF (ng/g) | HEPTA -CDF (ng/g) | OCTA -CDF (ng/g) | TOTAL -CDF (ng/g) | TCDD + TCDF (ng/g) |
|---|---|---|---|---|---|---|---|---|---|
| C | Perimeter Composite | 0.51 | 2.4 | 3.9 | 4 | 3.3 | 0.81 | 14.41 | 43.21 |
| D | Perimeter Composite | 1.3 | 11 | 7.7 | 5.3 | 2.7 | 0.61 | 27.31 | 48.01 |

analyzed. This was expected because the chemical properties of the PCDD compounds cause them to adhere strongly to the finest particles.

A review of the PCDF homolog concentrations in the fly ash again showed that the variability between the shifts and units was relatively small, while the concentration variability between facilities was extremely large (i.e., the concentration standard deviations for the homologs exceeded the average homolog concentrations). Facility C had the highest concentration of total PCDFs, as well as the highest concentration of each PCDF homolog, followed by Facility B, Facility D, and Facility A, which had the lowest concentration of each PCDF homolog. The hexa-CDF homolog was the most prevalent at three facilities, and the second most prevalent at the fourth facility. Similarly, the octa-CDF homolog was the least prevalent at three facilities and, the second least prevalent at the fourth facility. The tetra-CDF homolog was generally the second most prevalent, with the exception of Facility C where it was the least prevalent. As was the case for the PCDDs, the hexa- through octa-chlorinated classes of PCDFs increased disproportionately as the total PCDFs increased.

As was the case for the PCDDs, two discrete fly ash fractions from Facility C were analyzed for PCDFs. Again, the coarse fly ash fraction contained a minimal quantity of PCDFs, but the fine fly ash fraction exhibited the highest concentrations of PCDF homologs found in any fly ash sample. This was again anticipated because the PCDF compounds, acting similarly to the PCDD compounds, adhere strongly to the finest fly ash particles.

Upon comparing the concentrations of PCDDs with PCDFs in the fly ash, the following observations were noted. First, the total concentrations of PCDDs and PCDFs followed the same sequence of abundance among the facilities (i.e., the total concentrations of both PCDDs and PCDFs increased in the order: Facility A - Facility D - Facility B - Facility C). Second, the production of the hexa-chlorinated classes of PCDDs and PCDFs was favored at each of the four facilities. Third, the penta- and/or hepta-chlorinated classes of both PCDD and PCDF are never the most or least abundant. Finally, there does not appear to be any correlation between the relative abundances (i.e., percentage) of PCDDs or PCDFs in the total PCDD/PCDF concentrations.

A review of the PCDD homolog concentrations in the combined bottom/fly ash and bottom ash showed that the variability between shifts and units was relatively small compared to the variability between facilities. However, some trends for the variabilities between shifts and units were observed. At Facility A, variability between units was very small (i.e., the PCDD concentrations of the ash from the different units was essentially equal), but the PM shift samples contained higher PCDD concentrations than the AM shift samples. Similarly, at Facility B the PM shift samples exhibited higher PCDD concentrations than the AM shift samples, but at Facility B, the units also showed a difference with the samples from Unit 4 consistently having higher PCDD concentrations than those from Unit 3. At Facility C, the AM shift samples showed higher PCDD concentrations than the PM shift samples. Finally, at Facility D, the variability was very small without any notable trends between shifts.

As was the case for the fly ash, Facility C combined ash samples had the highest concentrations of individual PCDD homologs as well as total PCDDs. The samples from Facility A had the second highest PCDD concentrations, followed by the samples from Facilities D and B, sequentially. There was not any notable trends for the relative abundances of the individual PCDD homologs. For example, the penta-CDD homolog was the most abundant for Facilities A and D, while the octo-CDD and hepta-CDD homologs predominated at Facilities B and C, respectively. Similarly, the least abundant homolog was tetra-CDD for Facilities B, C, and D; however, the octa-CDD homolog, which was the most abundant at Facility B, was the least abundant at Facility A. The 2,3,7,8-TCDD isomer concentrations were very low for all four facilities, usually being only slightly above the detection limit.

A review of the PCDF homolog concentrations in the combined bottom/fly ash and bottom ash samples indicated that the variability between shifts and units was relatively large, and that the variability between facilities was extremely large. At Facility A, the samples from Unit 2 had higher PCDF concentrations than the samples from Unit 3, and the samples collected during the PM shifts had higher concentrations of PCDFs than those from the AM shifts. Similarly, at Facility B the Unit 4 samples exhibited higher PCDFs than the Unit 3 samples, and the PM shift samples contained more PCDFs than the AM shift samples. However, at Facility C, the AM shift samples contained five times more PCDFs than the PM shift samples. Finally, at Facility D the PCDF concentrations for the samples from each shift were essentially equal.

The combined ash samples from Facilities A and C had the highest concentrations of PCDFs and were approximately equal and were seven times lower than corresponding concentrations from Facilities A and C. The octa-CDF homolog was the least prevalent for three of the facilities; however, it was the second most abundant homolog for Facility B. This difference may be attributed to the Facility B sample consisting exclusively of bottom ash, while the samples from the other three facilities consisted of combined bottom/fly ash. The tetra- and hepta-CDF homologs predominated, each being the most abundant homolog at two facilities. The concentrations of the penta- and hexa-CDF homologs were approximately equal, and these homologs were never the most or least abundant at any facility. The 2,3,7,8-TCDF isomer accounted for 15 to 20 percent of the total tetra-CDF homologs.

Upon comparing the PCDD and PCDF concentrations in the combined and bottom ash, the following observations were noted. First, the variabilities between shifts and units followed the same patterns for PCDDs and PCDFs. Second, there was not any correlation between the most abundant or least abundant for PCDDs and PCDFs. That is, while the tetra-CDF homolog was the most abundant PCDF, the tetra-CDD homolog was the least abundant PCDD. One notable trend concerning the homologs was that the hexa-CDD and hexa-CDF homologs were never the most or least abundant. Third, as the total PCDDs increased, so did the total PCDFs. Consequently, the facilities that had the biggest concentrations of PCDDs had the highest concentrations of PCDFs, and this was also true for the facilities with the lowest concentrations. Finally, as was the case for the fly ash, there was not an apparent correlation or trend between the relative abundances of PCDDs or PCDFs in the total PCDD/PCDF concentrations.

A review of the landfill composite sample results for PCDDs showed that Facilities C and D were approximately equal. The tetra-CDD homolog was the least abundant at both facilities, and the hepta-CDD and penta-CDD homologs were the most abundant at Facilities C and D, respectively. The tetra-CDDs at each facility were approximately six percent 2,3,7,8-TCDD.

The PCDF results of the landfill composite samples showed that Facility D was two times higher than Facility C. The octa-CDF homolog was the least prevalent at each facility, and the hexa-CDF and tetra-CDF homologs were the most prevalent at Facilities C and D, respectively. There did not appear to be any trends concerning the concentrations of 2,3,7,8-TCDF, or the relative abundances of PCDD or PCDF in the total PCDD/PCDF concentrations.

Upon comparing the PCDD and PCDF results of the combined bottom/fly ash with the landfill perimeter composite samples from Facilities C and D, it was noted that the combined ash from Facility C contained six times more PCDDs and four times more PCDFs than the landfill composite. Conversely, at Facility D, the landfill composite sample contained two times more PCDDs and five times more PCDFs than the combined ash samples. The first observation indicates that the landfill composite sample at Facility C may have been biased by bottom ash, or that some of the PCDDs and PCDFs may have already leached from the landfill. The second observation suggests that the landfill composite sample at Facility D may have been biased by fly ash, which contained significantly more PCDDs and PCDFs than the bottom or combined ash. Similarly, both of these discrepancies may be attributed to the heterogeneity of the combined ash and disposed ash (i.e., landfill composite) samples.

Upon comparing the PCDD and PCDF results of the fly ash with the combined bottom/fly ash or bottom ash, the following observations were noted. First, the variability between facilities for both fly ash and combined/bottom ash PCDD and PCDF concentrations is extremely high. This indicates that the feed material and/or incinerator conditions at the four facilities are very different, resulting in the formation of significant quantities of PCDD/PCDFs at one facility, and the formation of negligible quantities of PCDD/PCDFs at another. Second, the variabilities between shifts and units for both PCDDs and PCDFs in the combined/bottom ash are greater than the corresponding variabilities for the fly ash. This discrepancy is caused by the heterogeneity of the combined/bottom ash compared to the homogeneity of the fly ash. Third, the fly ash from three facilities contained from three to forty times more PCDDs than the combined ash, and the fly ash from Facility B contained 120 times more PCDDs than the facility's bottom ash. This indicates that the PCDDs are associated with the fine fly ash particles and PCDD concentrations in the bottom ash are minimal. Therefore, the difference between the PCDD concentrations in the fly ash and combined ash is caused by a bottom ash dilution effect. Similarly, the fly ash from three facilities contained from two to 25 times more PCDFs than the combined ash, and the fly ash from Facility B contained 75 times more PCDFs than the facility's bottom ash. Therefore, the difference between PCDF concentrations in the combined ash and fly ash is a result of the dilution effect from the bottom ash. Fourth, the tetra-CDD homologs are the least prevalent in both the fly ash and the combined/bottom ash, while the hexa- through octo- chlorinated classes of PCDDs are the most prevalent. This suggests that the typical incinerator conditions favor the production of the more highly chlorinated PCDD species. However, for both the fly ash and combined/bottom ash, the tetra- through hexa-chlorinated species of PCDFs are the most abundant. This indicates that these same incinerator conditions favor the formation of the lower chlorinated species of PCDFs. Finally, the total concentrations of PCDDs and PCDFs in both fly ash and combined/bottom ash followed the same sequence of abundance among the facilities (i.e., the total concentrations of both PCDDs and PCDFs in fly ash and combined ash increased in the order: Facility A - Facility D - Facility B - Facility C).

## 4.3 Laboratory Leachates

One laboratory leachate composite sample of fly ash and one of bottom/fly or bottom ash (plus 25 percent field duplicates) were collected from each facility. These laboratory leachate composite samples were representative of all combustion units and shifts during which sampling was conducted.

The laboratory leachate composite samples from each facility were subjected to three different leaching procedures in an attempt to evaluate and compare the mobility of various constituents under different extraction conditions.. The three different laboratory leaching procedures were Extraction Procedure (EP), Toxicity Characteristic Leaching Procedure (TCLP), and Mono-filled Waste Extraction Procedure (MWEP; SW-924). The leachates prepared using these procedures were analyzed for metals and organic constituents. Additionally, the leachates prepared using TCLP were analyzed for PCDD/PCDF. The following sections present the analytical results for each parameter summarized by sample matrix, facility, and laboratory leaching procedure and a narrative evaluation of these results.

### 4.3.1 Metals

The laboratory leachates prepared by EP, TCLP, and MWEP were analyzed for cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), nickel (Ni), zinc (Zn), arsenic (As), selenium (Se), and mercury (Hg). The results of these analyses are tabulated and summarized by sample matrix, facility, and leachate procedure in Table 4.8. The MWEP method yielded two leachates from each laboratory leachate composite sample. These leachates are listed in Table 4.8 as EX1 (i.e., Extraction 1) and EX2 (i.e., Extraction 2).

Upon reviewing Table 4.8, the following observations were noted. First, the variability between leaching procedures and sample matrices appears to be much greater than the variability between facilities. Additionally, because of this variability, there does not appear to be any trends between the metal concentrations and the facilities. Second, zinc, iron, lead, and manganese were present in the highest concentrations in the leachates, while mercury was not present in any of the leachates. Third, the fly ash appeared to contain higher extractable quantities of cadmium and zinc than the bottom/fly and bottom ash, however the extractable quantities of chromium, iron, and lead in the bottom/fly and bottom ash were higher than in the fly ash. Finally, the extractable quantities of copper, manganese, nickel, arsenic, mercury, and selenium were essentially equal in the fly ash and the bottom/fly or bottom ash.

Upon comparing the different extraction procedures, the following observations were noted. First, the EP and TCLP extraction methods were much more aggressive than the MWEP for leaching every metal, except selenium. In fact, the MWEP method was the only extraction procedure which leached selenium. Second, none of the extraction methods leached mercury. Third, the EP method appeared to extract copper and zinc more vigorously than the TCLP method, while the TCLP method extracted chromium, iron, manganese, nickel, and arsenic more aggressively than the EP method. In fact, the TCLP method was the only one to extract arsenic. Fourth, the extraction efficiencies of EP and TCLP were approximately equal for cadmium, lead, and zinc. Finally, the concentrations of metals in SW924-EX1 were generally greater than those in SW924-EX2.

TABLE 4.8 EXTRACTABLE METALS DATA FOR THREE LABORATORY LEACHING PROCEDURES

| Leachate Procedure | Facility | Sample Matrix | Cd mg/L | Cr mg/L | Cu mg/L | Fe mg/L | Pb mg/L | Mn mg/L | Ni mg/L | Zn mg/L | As mg/L | Hg mg/L | Se mg/L |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| EP Tox | A | Bottom/Fly | 0.827 | 0.016 | 1.19 | 4.50 | 20.8 | 4.15 | 0.241 | 38.5 | <0.01 | <0.008 | <0.05 |
| TCLP | A | Bottom/Fly | 0.682 | 0.096 | 0.019 | 60.6 | 16.3 | 7.18 | 0.346 | 55.8 | 0.020 | <0.008 | <0.05 |
| SW924-EX1 | A | Bottom/Fly | <0.01 | <0.005 | <0.005 | <0.005 | <0.05 | <0.001 | <0.015 | <0.003 | <0.01 | <0.02 | <0.005 |
| SW924-EX2 | A | Bottom/Fly | <0.01 | <0.005 | <0.005 | <0.005 | <0.05 | <0.001 | <0.015 | 0.0031 | <0.01 | <0.02 | <0.005 |
| EP Tox | C | Bottom/Fly | 0.060 | 0.0059 | 0.039 | 143 | 2.09 | 4.11 | 0.337 | 726 | <0.01 | <0.008 | <0.05 |
| TCLP | C | Bottom/Fly | 3.32 | <0.005 | 0.0076 | 23.4 | 7.30 | 11.9 | 0.805 | 373 | <0.01 | <0.008 | <0.05 |
| SW924-EX1 | C | Bottom/Fly | <0.01 | <0.005 | 0.023 | 0.038 | 0.063 | 0.0021 | <0.015 | 0.067 | <0.01 | <0.02 | <0.05 |
| SW924-EX2 | C | Bottom/Fly | <0.01 | <0.005 | <0.005 | 0.015 | <0.05 | <0.001 | <0.015 | 0.051 | <0.01 | <0.02 | <0.005 |
| EP Tox | D | Bottom/Fly | 0.649 | 0.033 | 0.051 | 66.4 | 7.26 | 6.24 | 0.415 | 61.7 | <0.01 | <0.008 | <0.05 |
| TCLP | D | Bottom/Fly | 0.025 | <0.005 | <0.005 | 0.828 | 0.655 | 4.20 | 0.573 | 23.3 | <0.01 | <0.008 | <0.005 |
| SW924-EX1 | D | Bottom/Fly | <0.01 | 0.005 | 0.070 | <0.005 | <0.05 | <0.001 | <0.015 | <0.003 | <0.01 | <0.02 | <0.005 |
| SW924-EX2 | D | Bottom/Fly | <0.01 | <0.005 | 0.009 | 0.01 | <0.05 | <0.001 | <0.015 | 0.0034 | <0.01 | <0.02 | <0.005 |
| EP Tox | B | Bottom | 0.388 | 0.150 | 0.127 | 21.0 | 34.0 | 3.60 | 0.250 | 58.4 | <0.01 | <0.008 | <0.05 |
| TCLP | B | Bottom | 0.418 | 0.439 | 0.018 | 52.8 | 30.1 | 6.82 | 0.473 | 83.2 | 0.037 | <0.008 | <0.05 |
| SW924-EX1 | B | Bottom | <0.01 | <0.005 | 0.0089 | <0.005 | <0.05 | <0.001 | <0.015 | <0.003 | <0.01 | <0.02 | <0.025 |
| SW924-EX2 | B | Bottom | <0.01 | <0.005 | <0.005 | 0.024 | <0.05 | 0.0012 | <0.015 | 0.018 | <0.01 | <0.02 | <0.005 |
| EP Tox | A | Fly | 6.02 | <0.005 | 0.045 | <0.005 | 4.72 | 6.62 | 0.326 | 186 | <0.01 | <0.008 | <0.05 |
| EP Tox | A | Fly (Dup.) | 7.72 | <0.005 | 0.254 | 0.007 | 10.8 | 8.03 | 0.466 | 262 | <0.01 | <0.008 | <0.05 |
| TCLP | A | Fly | 0.015 | 0.136 | <0.005 | 190 | 0.962 | 4.62 | 0.372 | 77.6 | 0.024 | <0.008 | <0.025 |
| TCLP | A | Fly (Dup.) | 0.032 | <0.005 | 0.116 | <0.005 | <0.05 | 0.049 | <0.015 | 0.151 | <0.01 | <0.008 | <0.05 |
| SW924-EX1 | A | Fly | <0.015 | 0.010 | 0.027 | 0.167 | <0.075 | 0.0058 | 0.0225 | 0.026 | <0.01 | <0.04 | <0.05 |
| SW924-EX1 | A | Fly (Dup.) | <0.01 | <0.005 | 0.089 | <0.005 | <0.05 | 0.0017 | <0.015 | 0.045 | <0.01 | <0.02 | <0.005 |
| SW924-EX2 | A | Fly | <0.01 | <0.005 | 0.009 | 0.057 | 0.072 | 0.003 | <0.015 | 0.083 | <0.01 | <0.02 | <0.005 |
| SW924-EX2 | A | Fly (Dup.) | <0.01 | <0.005 | <0.005 | <0.005 | <0.05 | <0.001 | <0.015 | <0.003 | <0.01 | <0.02 | <0.005 |
| EP Tox | B | Fly | 18.0 | <0.005 | 0.171 | 0.060 | 19.3 | 4.65 | 0.137 | 726 | <0.01 | <0.008 | <0.05 |
| TCLP | B | Fly | 17.2 | <0.005 | 0.078 | 0.019 | 6.91 | 3.97 | 0.076 | 275 | <0.01 | <0.008 | <0.05 |
| SW924-EX1 | B | Fly | <0.01 | 0.0086 | <0.005 | <0.005 | <0.05 | 0.0024 | <0.015 | 0.026 | <0.01 | <0.02 | <0.05 |
| SW924-EX2 | B | Fly | 0.033 | 0.01 | 0.012 | 0.118 | 0.148 | 0.0052 | <0.015 | 1.2 | <0.01 | <0.02 | <0.025 |
| EP Tox | C | Fly | 7.89 | 0.038 | 1.62 | 0.490 | 17.8 | 2.71 | 1.92 | 362 | <0.01 | <0.008 | <0.05 |
| TCLP | C | Fly | 8.36 | 0.129 | 0.201 | 34.2 | 13.4 | 5.14 | 1.52 | 446 | 0.036 | <0.008 | <0.025 |
| SW924-EX1 | C | Fly | 0.122 | 0.0060 | 0.045 | 0.067 | 0.128 | 0.014 | <0.015 | 1.22 | <0.01 | <0.02 | 0.108 |
| SW924-EX2 | C | Fly | <0.01 | <0.005 | <0.005 | <0.005 | <0.05 | <0.001 | <0.015 | <0.003 | <0.01 | <0.02 | <0.025 |
| EP Tox | D | Fly | 8.60 | <0.005 | 0.041 | 0.012 | 19.6 | 6.74 | 0.288 | 430 | <0.01 | <0.008 | <0.05 |
| EP Tox | D | Fly (Dup.) | 9.18 | <0.005 | 0.131 | 0.0074 | 25.2 | 7.6 | 0.284 | 458 | <0.01 | <0.008 | <0.05 |
| TCLP | D | Fly | 10.3 | 0.487 | 0.018 | 12.8 | 15.2 | 14.7 | 0.582 | 746 | 0.086 | <0.008 | <0.05 |
| TCLP | D | Fly (Dup.) | 8.90 | 0.544 | 0.0059 | 15.0 | 12.8 | 13.6 | 0.567 | 624 | 0.111 | <0.008 | <0.005 |
| SW924-EX1 | D | Fly | 0.015 | 0.071 | 0.0052 | <0.005 | <0.05 | 0.0061 | <0.015 | 0.180 | <0.01 | <0.02 | 0.047 |
| SW924-EX1 | D | Fly (Dup.) | <0.01 | 0.114 | 0.0051 | <0.005 | <0.05 | <0.001 | 0.022 | 0.036 | <0.01 | <0.02 | <0.05 |
| SW924-EX2 | D | Fly | <0.01 | 0.116 | <0.005 | <0.005 | <0.05 | 0.002 | <0.015 | 0.018 | <0.01 | <0.02 | <0.025 |
| SW924-EX2 | D | Fly (Dup.) | <0.01 | 0.15 | <0.005 | <0.005 | <0.05 | <0.001 | <0.015 | 0.02 | <0.01 | <0.02 | <0.025 |

TABLE 4.8 EXTRACTABLE METALS DATA FOR THREE LABORATORY LEACHING PROCEDURES

| Leachate Procedure | Sample Type | Summary Statistics | Cd mg/L | Cr mg/L | Cu mg/L | Fe mg/L | Pb mg/L | Mn mg/L | Ni mg/L | Zn mg/L | As mg/L | Hg mg/L | Se mg/L |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| EP Tox | Combined Bottom/ Fly Ash | Min. | 0.06 | 0.0059 | 0.039 | 4.5 | 2.09 | 3.6 | 0.241 | 38.5 | 0.005 | 0.004 | 0.025 |
| | | Max. | 0.827 | 0.15 | 1.19 | 143 | 34 | 6.24 | 0.415 | 726 | 0.005 | 0.004 | 0.025 |
| | | Avg. | 0.481 | 0.051 | 0.352 | 58.725 | 16.038 | 4.525 | 0.311 | 221.150 | 0.005 | 0.004 | 0.025 |
| | | Std Dev | 0.289 | 0.058 | 0.485 | 53.677 | 12.419 | 1.014 | 0.071 | 291.610 | 0.000 | 0.000 | 0.000 |
| TCLP | Combined Bottom/ Fly Ash | Min. | 0.025 | 0.0025 | 0.0025 | 0.828 | 0.655 | 4.2 | 0.346 | 23.3 | 0.005 | 0.004 | 0.0025 |
| | | Max. | 3.32 | 0.439 | 0.019 | 60.6 | 30.1 | 11.9 | 0.805 | 373 | 0.037 | 0.004 | 0.025 |
| | | Avg. | 1.111 | 0.135 | 0.012 | 34.407 | 13.589 | 7.525 | 0.549 | 133.825 | 0.017 | 0.004 | 0.019 |
| | | Std Dev | 1.296 | 0.180 | 0.007 | 23.838 | 11.032 | 2.775 | 0.168 | 139.706 | 0.013 | 0.000 | 0.010 |
| SW 924 Extract 1 | Combined Bottom/ Fly Ash | Min. | 0.005 | 0.0025 | 0.0025 | 0.0025 | 0.025 | 0.0005 | 0.0075 | 0.0015 | 0.005 | 0.01 | 0.0025 |
| | | Max. | 0.005 | 0.005 | 0.07 | 0.038 | 0.063 | 0.0021 | 0.0075 | 0.067 | 0.005 | 0.01 | 0.025 |
| | | Avg. | 0.005 | 0.003 | 0.026 | 0.011 | 0.035 | 0.001 | 0.008 | 0.018 | 0.005 | 0.010 | 0.011 |
| | | Std Dev | 0.000 | 0.001 | 0.026 | 0.015 | 0.016 | 0.001 | 0.000 | 0.028 | 0.000 | 0.000 | 0.009 |
| SW 924 Extract 2 | Combined Bottom/ Fly Ash | Min. | 0.005 | 0.0025 | 0.0025 | 0.0025 | 0.025 | 0.0005 | 0.0075 | 0.0031 | 0.005 | 0.01 | 0.0025 |
| | | Max. | 0.005 | 0.0025 | 0.009 | 0.024 | 0.025 | 0.0012 | 0.0075 | 0.051 | 0.005 | 0.01 | 0.0025 |
| | | Avg. | 0.005 | 0.003 | 0.004 | 0.013 | 0.025 | 0.001 | 0.008 | 0.019 | 0.005 | 0.010 | 0.003 |
| | | Std Dev | 0.000 | 0.000 | 0.003 | 0.008 | 0.000 | 0.000 | 0.000 | 0.020 | 0.000 | 0.000 | 0.000 |
| EP Tox | Fly Ash | Min. | 6.02 | 0.0025 | 0.041 | 0.0025 | 4.72 | 2.71 | 0.137 | 186 | 0.005 | 0.004 | 0.025 |
| | | Max. | 18 | 0.038 | 1.62 | 0.49 | 25.2 | 8.03 | 1.92 | 726 | 0.005 | 0.004 | 0.025 |
| | | Avg. | 9.568 | 0.008 | 0.377 | 0.096 | 16.237 | 6.058 | 0.570 | 404.000 | 0.005 | 0.004 | 0.025 |
| | | Std Dev | 3.895 | 0.013 | 0.561 | 0.177 | 6.654 | 1.837 | 0.611 | 171.624 | 0.000 | 0.000 | 0.000 |
| TCLP | Fly Ash | Min. | 0.015 | 0.0025 | 0.0025 | 0.0025 | 0.025 | 0.049 | 0.0075 | 0.151 | 0.005 | 0.004 | 0.0025 |
| | | Max. | 17.2 | 0.544 | 0.201 | 190 | 15.2 | 14.7 | 1.52 | 746 | 0.111 | 0.004 | 0.025 |
| | | Avg. | 7.468 | 0.217 | 0.070 | 42.004 | 8.216 | 7.013 | 0.521 | 361.459 | 0.045 | 0.004 | 0.017 |
| | | Std Dev | 6.006 | 0.218 | 0.072 | 67.172 | 6.029 | 5.315 | 0.498 | 271.582 | 0.040 | 0.000 | 0.009 |
| SW 924 Extract 1 | Fly Ash | Min. | 0.005 | 0.0025 | 0.0025 | 0.0025 | 0.025 | 0.0005 | 0 | 0.026 | 0.005 | 0.01 | 0.0025 |
| | | Max. | 0.122 | 0.114 | 0.089 | 0.167 | 0.128 | 0.014 | 0.022 | 1.22 | 0.005 | 0.02 | 0.108 |
| | | Avg. | 0.027 | 0.035 | 0.029 | 0.041 | 0.044 | 0.005 | 0.009 | 0.256 | 0.005 | 0.012 | 0.039 |
| | | Std Dev | 0.043 | 0.042 | 0.031 | 0.061 | 0.038 | 0.004 | 0.007 | 0.435 | 0.000 | 0.004 | 0.034 |
| SW 924 Extract 2 | Fly Ash | Min. | 0.005 | 0.0025 | 0.0025 | 0.0025 | 0.025 | 0.0005 | 0.0075 | 0.0015 | 0.005 | 0.01 | 0.0025 |
| | | Max. | 0.033 | 0.15 | 0.012 | 0.118 | 0.148 | 0.0052 | 0.0075 | 1.2 | 0.005 | 0.01 | 0.0125 |
| | | Avg. | 0.010 | 0.047 | 0.005 | 0.031 | 0.053 | 0.002 | 0.008 | 0.221 | 0.005 | 0.010 | 0.009 |
| | | Std Dev | 0.010 | 0.061 | 0.004 | 0.044 | 0.046 | 0.002 | 0.000 | 0.439 | 0.000 | 0.000 | 0.005 |

TABLE 4.8 EXTRACTABLE METALS DATA FOR THREE LABORATORY LEACHING PROCEDURES

LEGEND:

EP TOX = EP TOXICITY extraction procedure
TCLP = TOTAL CHARACTERISTIC LEACHATE PROCEDURE
SW 924 = Procedure for estimating monofilled solid waste leachate composition
SW 924 EX1 = First extract using SW 924 procedure
SW 924 EX2 = Second extract (on the same sample) using SW 924 procedure
Bottom/Fly = combined bottom ash and fly ash samples
Fly = Fly ash
Bottom = Bottom ash
Dup. = Duplicate (split) of the previous sample

### 4.3.2 Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzo-furans

The laboratory leachate samples prepared by TCLP were analyzed for PCDD and PCDF homologs in the tetra- through octa-chlorinated classes. Additionally, the 2,3,7,8-TCDD and 2,3,7,8-TCDF isomers were identified and quantified. The results of these analyses are summarized by facility in Table 4.9.

A review of the PCDD and PCDF concentrations in the TCLP-prepared leachates showed that the extracted concentrations of PCDDs and PCDFs were approximately equal. Only the hepta-CDD and octa-CDD homologs were detected in two fly ash leachates (Facilities A and B), and only the octa-CDD homolog was detected in one bottom ash leachate (Facility B). Similarly, the hepta-CDF and octa-CDF homologs were detected in one fly ash leachate (Facility B), while only the hepta-CDF homolog was detected in the Facility A fly ash leachate. The octa-CDF homolog was detected in only one bottom ash leachate (Facility B). Because the solid samples contained significantly more PCDD and PCDF homologs than the TCLP-prepared leachates, these observations indicate that the TCLP method is inefficient for extracting (i.e., leaching) PCDD and PCDF compounds in a waste ash matrix. Furthermore, they indicate that only the highly chlorinated PCDD and PCDF species (i.e., hepta- and octa) tended to be extracted by TCLP.

### 4.3.3 Organic Constituents

The laboratory leachates prepared by EP, TCLP, and SW-924 (MWEP) were analyzed for organic constituents (i.e., organic scan and BNAs). Additionally, the leachates prepared by MWEP were analyzed for TOC. The results of these analyses are summarized by facility and extraction procedure in Table 4.10. The numerical code appearing with each organic constituent name represents the CAS designation for that compound.

## TABLE 4.9 PCDD AND PCDF IN LABORATORY LEACHATE SAMPLES (TCLP)

### DIOXIN HOMOLOGS

| Plant | Sample Matrix | Sample Description | 2,3,7,8 TCDD (ng/l) | TETRA -CDD (ng/l) | PENTA -CDD (ng/l) | HEXA -CDD (ng/l) | HEPTA -CDD (ng/l) | OCTA -CDD (ng/l) | TOTAL -CDD (ng/l) |
|---|---|---|---|---|---|---|---|---|---|
| A | Bottom/Fly | Unit 2, 9/26, AM | <0.038 | <0.038 | <0.023 | <0.018 | <0.028 | <0.035 | 0 |
| A | Fly | Unit 2, 9/26, AM | <0.056 | <0.056 | <0.056 | <0.026 | 0.11 | 0.078 | 0.188 |
| B | Bottom | Unit 4, 9/28, AM | <0.076 | <0.076 | <0.027 | <0.015 | <0.120 | 0.091 | 0.091 |
| B | Fly | Unit 4, 9/28, AM | <0.072 | <0.072 | <0.040 | <0.027 | 0.036 | 0.11 | 0.146 |
| C | Bottom/Fly | Unit 2, 9/29, PM | <0.065 | <0.065 | <0.067 | <0.022 | <0.049 | <0.100 | 0 |
| C | Fly | Unit 2, Coarse | <0.094 | <0.094 | <0.042 | <0.019 | <0.079 | <0.130 | 0 |
| D | Bottom/Fly | Unit 1-2, 10/3, AM | <0.230 | <0.230 | <0.060 | <0.044 | <0.100 | <0.230 | 0 |
| D | Fly | Unit 1-2, 10/3, AM | <0.071 | <0.071 | <0.048 | <0.022 | <0.038 | <0.140 | 0 |

### FURAN HOMOLOGS

| Plant | Sample Matrix | Sample Description | 2,3,7,8 TCDF (ng/l) | TETRA -CDF (ng/l) | PENTA -CDF (ng/l) | HEXA -CDF (ng/l) | HEPTA -CDF (ng/l) | OCTA -CDF (ng/l) | TOTAL -CDF (ng/l) |
|---|---|---|---|---|---|---|---|---|---|
| A | Bottom/Fly | Unit 2, 9/26, AM | <0.031 | <0.031 | <0.013 | <0.008 | <0.013 | <0.060 | 0 |
| A | Fly | Unit 2, 9/26, AM | <0.120 | <0.120 | <0.019 | <0.015 | 0.049 | <0.081 | 0.049 |
| B | Bottom | Unit 4, 9/28, AM | <0.040 | <0.040 | <0.013 | <0.022 | <0.043 | 0.054 | 0.054 |
| B | Fly | Unit 4, 9/28, AM | <0.052 | <0.052 | <0.026 | <0.020 | 0.063 | 0.089 | 0.152 |
| C | Bottom/Fly | Unit 2, 9/29, PM | <0.064 | <0.064 | <0.020 | <0.020 | <0.024 | <0.130 | 0 |
| C | Fly | Unit 2, Coarse | <0.077 | <0.077 | <0.026 | <0.014 | <0.030 | <0.100 | 0 |
| D | Bottom/Fly | Unit 1-2, 10/3, AM | <0.200 | <0.200 | <0.042 | <0.025 | <0.035 | <0.260 | 0 |
| D | Fly | Unit 1-2, 10/3, AM | <0.048 | <0.048 | <0.016 | <0.013 | <0.020 | <0.015 | 0 |

## TABLE 4.10 EXTRACTABLE ORGANICS DATA FOR THREE LEACHING PROCEDURES

### EP Toxicity

| Plant | Sample Matrix | Organic Scan (mg/l) | BNA Peaks Found (No.) | Naphth-alene 91203 (ug/l) | Methyl Naphtha. 91576 (ug/l) | Diethyl-phthalate 84662 (ug/l) | Dimethyl pro'diol 126307 (ug/l) | Methyoxy Ethane 74498887 (ug/l) | Number of Unknown Organics |
|---|---|---|---|---|---|---|---|---|---|
| A | Bottom/Fly | <0.25 | 5 | 8 | 18 | 16 | | | 2 |
| A | Fly | <0.25 | | | | | | | |
| A | Fly (Dup) | <0.25 | | | | | | | |
| B | Bottom | <0.25 | 6 | | | 13 | | 12 | 4 |
| B | Fly | <0.25 | 6 | | | 15 | | | 5 |
| C | Bottom/Fly | <0.25 | 4 | | | 9 | | | 4 |
| C | Fly | <0.25 | 3 | | | 18 | | | 2 |
| D | Bottom/Fly | <0.25 | 4 | | | 16 | 190 | | 2 |
| D | Fly | <0.25 | 5 | | | 17 | | | 4 |
| D | Fly (Dup) | <0.25 | | | | | | | |
| TOTAL NUMBER FOUND | | | 33 | 1 | 1 | 7 | 1 | 1 | 23 |

### TCLP

| Plant | Sample Matrix | Organic Scan (mg/l) | BNA Peaks Found (No.) | Diethyl-phthal. 84662 (ug/l) | Dibutyl-phthal. 84742 (ug/l) | bis E.H. phthal. 117817 (ug/l) | Methyoxy Ethane 74498887 (ug/l) | Methoxy Ethanol 111773 (ug/l) | Dimethyl Prop'diol 126307 (ug/l) | Number of Unknown Organics |
|---|---|---|---|---|---|---|---|---|---|---|
| A | Bottom/Fly | 6.9 | 12 | 21 | | | | | | 11 |
| A | Fly | <0.25 | | | | | | | | |
| A | Fly (Dup) | <0.25 | | | | | | | | |
| B | Bottom | <0.25 | 21 | 11 | 5 | | 22 | | | 19 |
| B | Fly | <0.25 | | | | | | | | |
| C | Bottom/Fly | <0.25 | 17 | 16 | 4 | | | 13 | | 14 |
| C | Fly | <0.25 | 14 | 13 | | 4 | | 10 | | 11 |
| D | Bottom/Fly | <0.25 | 14 | 10 | 4 | | | | 140 | 11 |
| D | Fly | <0.25 | 12 | 12 | | | 10 | | | 10 |
| D | Fly (Dup) | <0.25 | | | | | | | | |
| TOTAL NUMBER FOUND | | | 90 | 6 | 3 | 1 | 2 | 2 | 1 | 76 |

## TABLE 4.10 EXTRACTABLE ORGANICS DATA FOR THREE LEACHING PROCEDURES

### SW 924 FIRST EXTRACTION

| Plant | Sample Matrix | TOC (mg/l) | Organic Scan (mg/l) | BNA Peaks Found (No.) | Phenol 108952 (ug/l) | Benzoic Acid 65850 (ug/l) | Diethyl-phthalate 84662 (ug/l) | E., DiM Dioxane 25796263 (ug/l) | Dimethyl pro'diol 126307 (ug/l) | Bis oxy Ethanol 112276 (ug/l) |
|---|---|---|---|---|---|---|---|---|---|---|
| A | Bottom/Fly | 9.4 | <0.25 | 11 | | | | | | 96 |
| A | Fly | 4.8 | <0.25 | | | | | | | |
| A | Fly (Dup) | 6.8 | <0.25 | | | | | | | |
| B | Bottom | 12.1 | <0.25 | 23 | 28 | 46 | | | | |
| B | Fly | 16.9 | <0.25 | | | | | | | |
| C | Bottom/Fly | 10.3 | <0.25 | 10 | | | | | | |
| C | Fly | 9.2 | <0.25 | | | | | | | |
| D | Bottom/Fly | 31 | <0.25 | 6 | | | 8 | 510 | 160 | |
| D | Fly | 6.7 | <0.25 | | | | | | | |
| D | Fly (Dup) | 4.4 | <0.25 | | | | | | | |
| TOTAL NUMBER FOUND | | | | 50 | 1 | 1 | 1 | 1 | 1 | 1 |

| Plant | Sample Matrix | Oleyl Alcohol 143282 (ug/l) | Ethoxy Ethanol 929373 (ug/l) | Cycloocta Decane 17455139 (ug/l) | Methoxy Ethane 74498887 (ug/l) | M.Furan-dione 766392 (ug/l) | SW 924 Extr. 1 Unknowns (No.) |
|---|---|---|---|---|---|---|---|
| A | Bottom/Fly | 88 | 310 | 580 | | | 4 |
| A | Fly | | | | | | |
| A | Fly (Dup) | | | | | | |
| B | Bottom | | | 150 | 10 | 6 | 17 |
| B | Fly | | | | | | |
| C | Bottom/Fly | | | | | | 10 |
| C | Fly | | | | | | |
| D | Bottom/Fly | | | | | | 3 |
| D | Fly | | | | | | |
| D | Fly (Dup) | | | | | | |
| TOTAL NUMBER FOUND | | 1 | 1 | 2 | 1 | 1 | 34 |

## TABLE 4.10 EXTRACTABLE ORGANICS DATA FOR THREE LEACHING PROCEDURES

### SW 924 SECOND EXTRACTION

| Plant | Sample Matrix | SW 924 Extr. 2 TOC (mg/l) | SW 924 Extr. 2 Org Scan (mg/l) | BNA Peaks Found (No.) | Phenol 108952 (ug/l) | Diethyl phthal. 84662 (ug/l) | E,hexyl phthal. 117817 (ug/l) | Dimethyl pro'diol 126307 (ug/l) | Methoxy Ethanol 111773 (ug/l) |
|---|---|---|---|---|---|---|---|---|---|
| A | Bottom/Fly | 6.7 | <0.25 | 13 | | | | | 6 |
| A | Fly | 6.3 | <0.25 | | | | | | |
| A | Fly (Dup) | 8.9 | <0.25 | | | | | | |
| B | Bottom | 8.5 | <0.25 | 21 | | | | | 13 |
| B | Fly | 7.0 | <0.25 | | | | | | |
| C | Bottom/Fly | 3.6 | <0.25 | 8 | | | | | |
| C | Fly | NA | <0.25 | | | | | | |
| D | Bottom/Fly | NA | <0.25 | 15 | 33 | 8 | 6 | 140 | |
| D | Fly | 9.3 | <0.25 | | | | | | |
| D | Fly (Dup) | 17.6 | <0.25 | | | | | | |
| | TOTAL NUMBER FOUND | | | 57 | 1 | 1 | 1 | 1 | 2 |

| Plant | Sample Matrix | Bis oxy Ethanol 112276 (ug/l) | Ethoxy Ethanol 929373 (ug/l) | Benz,Di Carboxy.A 117828 (ug/l) | Cycloocta decane 17455139 (ug/l) | Phenoxy Ethanol 2315619 (ug/l) | Oxahexa-decanol 23778521 (ug/l) | Unknowns (No.) |
|---|---|---|---|---|---|---|---|---|
| A | Bottom/Fly | 18 | 390 | 2 | 1200 | | | 6 |
| A | Fly | | | | | | | |
| A | Fly (Dup) | | | | | | | |
| B | Bottom | 46 | | | 950 | 17 | 13 | 15 |
| B | Fly | | | | | | | |
| C | Bottom/Fly | | | | | | | 8 |
| C | Fly | | | | | | | |
| D | Bottom/Fly | | | | | | | 11 |
| D | Fly | | | | | | | |
| D | Fly (Dup) | | | | | | | |
| TOTAL NUMBER FOUND | | 2 | 1 | 1 | 2 | 1 | 1 | 40 |

NOTE:

Names of organic constituents abbreviated ;
CAS numbers provided with constituent names

The results for the EP-prepared leachates showed that the organic scan did not detect any significant petroleum hydrocarbons in the samples from any of the facilities. The results also showed that similar BNAs were detected in samples from each facility with approximately equal concentrations. Furthermore, every EP leachate that had a quantifiable BNA contained diethylphthalate, which was the predominant BNA. Phthalate esters, such as the one described, are common plasticizers which were also noted in the laboratory leachate blank samples and therefore may represent a background interference. The BNAs appeared to be slightly more abundant in the bottom/fly ash than in the fly ash.

A review of the TCLP-prepared leachate results showed that gross measurement of petroleum hydrocarbon content was in one organic scan analysis (bottom/fly ash, Facility A). The other TCLP-prepared leachate results showed the same trends described above for the EP-prepared leachates.

The results presented in Table 4.10 for the SW-924 leachates showed that there was not a predominant BNA compound. The results also indicated that the bottom/fly ash and bottom ash contained slightly more leachable BNAs than the fly ash. Finally, the results showed that there was essentially no difference between the first and second SW-924 extractions.

Upon comparing the results from the three different leaching procedures, the following observations were noted. First, the TCLP method appears to be more efficient for extracting BNAs than the EP method (i.e., 90 BNA constituents were detected in the TCLP leachates, and only 33 BNAs were detected in the EP leachates). However, for the compounds that were extracted by both procedures (e.g., diethylphthalate), the concentrations were approximately equal. Second, the extraction efficiency for SW-924 procedure appears to lie between the EP and TCLP methods. However, the SW-924 procedure extracted totally different classes of BNA constituents than the EP and TCLP methods. Finally, for all three procedures, the combined bottom/fly ash and bottom ash contained slightly more BNAs than their corresponding fly ash, suggesting that the BNA compounds are associated with the coarser, heavier bottom ash materials or may be completely destroyed as the fly ash passes through high temperature zones in the incinerator.

### 4.4 Field Water Samples

The field water samples collected from each facility included: ground water, quench water, and field leachate. Each of these samples were analyzed for total metals, PCBs, and BNAs. Additionally, the quench water and field leachate samples were analyzed for PCDD/PCDFs. The ground water samples were not analyzed for PCDD/PCDFs because these materials generally absorb onto solid matrices which would not be expected to migrate through the soil/ground-water interface. Sections 4.4.1 through 4.4.4 present the analytical results of each parameter for these samples summarized by sample matrix and facility, and a narrative evaluation of the results.

### 4.4.1 Metals

The field leachates, ground water, and quench water samples were analyzed for total cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), nickel (Ni), zinc (Zn), arsenic (As), selenium (Se), and mercury (Hg). The results of these analyses were summarized by sample matrix and facility and are presented in Table 4.11.

A review of the field leachate data in Table 4.11 showed that the variability between samples at each facility, as well as the variability between facilities, is relatively high. However, the variability between samples at Facility D was lower than that at the other two facilities. In general, Facility C leachates contained the highest concentrations of metals, while the leachates at Facility B contained the lowest concentrations of metals. Iron was the most prevalent metal tested, while mercury and selenium were the least concentrated metals.

A review of the ground water data indicated that the variabilities between samples and facilities were relatively small. Furthermore, the

## TABLE 4.11 TOTAL METALS DATA FOR FIELD WATER SAMPLES

### FIELD LEACHATES

| Facility | Sample Description | Cd (mg/L) | Cr (mg/L) | Cu (mg/L) | Fe (mg/L) | Pb (mg/L) | Mn (mg/L) | Ni (mg/L) | Zn (mg/L) | As (mg/L) | Se (mg/L) | Hg (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| B | East Side | <0.010 | <0.005 | 0.112 | 0.758 | 0.050 | 0.105 | <0.015 | 0.048 | <0.010 | <0.005 | <0.0002 |
| B | North Side | <0.010 | <0.005 | 0.089 | 3.92 | 0.050 | 0.456 | 0.015 | 0.099 | <0.010 | <0.025 | 0.0002 |
| B | Northeast Corner | 0.044 | 0.024 | 0.091 | 34.5 | 0.206 | 4.57 | 0.039 | 0.098 | <0.010 | <0.005 | 0.0023 |
|  | FACILITY B AVERAGE | 0.0180 | 0.0097 | 0.0973 | 13.0593 | 0.0853 | 1.7103 | 0.0205 | 0.0817 | 0.0050 | 0.0058 | 0.0009 |
|  | STANDARD DEVIATION | 0.0184 | 0.0101 | 0.0104 | 15.2157 | 0.0853 | 2.0272 | 0.0134 | 0.0238 | 0.0000 | 0.0047 | 0.0010 |
| C | North Side | <0.010 | 0.011 | 0.2 | 12.9 | 0.068 | 0.244 | 0.027 | 0.346 | 0.017 | <0.025 | 0.00021 |
| C | Northeast Corner | <0.050 | 0.914 | 2.57 | 121 | 2.92 | 2.13 | 0.412 | 1.32 | 0.218 | 0.037 | 0.0080 |
| C | Northwest Corner | <0.010 | 0.0053 | 0.045 | 0.832 | 0.025 | 0.103 | <0.015 | 0.412 | 0.013 | <0.025 | <0.0002 |
|  | FACILITY C AVERAGE | 0.0117 | 0.3101 | 0.9383 | 44.9107 | 1.0043 | 0.8257 | 0.1488 | 0.6927 | 0.0827 | 0.0207 | 0.0028 |
|  | STANDARD DEVIATION | 0.0094 | 0.4270 | 1.1555 | 54.0284 | 1.3547 | 0.9241 | 0.1863 | 0.4444 | 0.0957 | 0.0115 | 0.0037 |
| D | Northeast Corner | 0.031 | 0.13 | 0.762 | 51.4 | 1.33 | 0.431 | 0.156 | 3.3 | 0.027 | <0.025 | 0.00079 |
| D | Northeast Corner, Dup | 0.023 | 0.099 | 0.603 | 45.2 | 0.925 | 0.369 | 0.149 | 2.69 | 0.025 | <0.025 | 0.00061 |
| D | Southeast Corner | <0.005 | 0.069 | 0.222 | 8.03 | 0.214 | 0.214 | 0.117 | 0.624 | 0.011 | <0.005 | <0.0002 |
|  | FACILITY D AVERAGE | 0.0188 | 0.0993 | 0.5290 | 34.8767 | 0.8230 | 0.3380 | 0.1407 | 2.2047 | 0.0210 | 0.0092 | 0.0005 |
|  | STANADARD DEVIATION | 0.0120 | 0.0249 | 0.2266 | 19.1515 | 0.4613 | 0.0913 | 0.0170 | 1.1451 | 0.0071 | 0.0047 | 0.0003 |
|  | TOTAL NUMBER | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 |
|  | MINIMUM | 0.0025 | 0.0025 | 0.045 | 0.758 | 0.025 | 0.103 | 0.0075 | 0.048 | 0.005 | 0.0025 | 0.0001 |
|  | MAXIMUM | 0.044 | 0.914 | 2.57 | 121 | 2.92 | 4.57 | 0.412 | 3.3 | 0.218 | 0.037 | 0.008 |
|  | OVERALL AVERAGE | 0.0162 | 0.1397 | 0.522 | 30.949 | 0.638 | 0.958 | 0.1033 | 0.993 | 0.0362 | 0.0119 | 0.0014 |
|  | STANDARD DEVIATION | 0.0142 | 0.2773 | 0.762 | 36.732 | 0.918 | 1.407 | 0.1231 | 1.140 | 0.0647 | 0.0100 | 0.0024 |

## TABLE 4.11 TOTAL METALS DATA FOR FIELD WATER SAMPLES

### QUENCH WATER

| Facility | Sample Description | Cd (mg/L) | Cr (mg/L) | Cu (mg/L) | Fe (mg/L) | Pb (mg/L) | Mn (mg/L) | Ni (mg/L) | Zn (mg/L) | As (mg/L) | Se (mg/L) | Hg (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A | Unit 1, 9/26 | 0.065 | 0.018 | 0.117 | 1.21 | 4.07 | 0.144 | <0.018 | 4.69 | <0.010 | <0.0125 | 0.0054 |
| A | Unit 2, 9/26 | 0.114 | 0.013 | 0.253 | 1.75 | 5.94 | 0.127 | <0.018 | 6.26 | 0.017 | <0.0125 | 0.018 |
|  | FACILITY A AVERAGE | 0.0895 | 0.0155 | 0.185 | 1.48 | 5.005 | 0.1355 | 0.009 | 5.475 | 0.011 | 0.005 | 0.0117 |
|  | STANDARD DEVIATION | 0.0245 | 0.0025 | 0.068 | 0.27 | 0.935 | 0.0085 | 0 | 0.785 | 0.006 | 0 | 0.0063 |
| B | Unit 3, 9/28 | <0.005 | 0.04 | 0.02 | 0.037 | 0.176 | 0.024 | <0.018 | 0.087 | <0.010 | <0.0125 | <0.0002 |
| B | Unit 4, 9/28 | <0.005 | 0.0085 | 0.048 | 0.409 | 0.274 | 0.082 | <0.018 | 0.218 | <0.010 | <0.0125 | 0.001 |
| B | Unit 4, 9/28, Dup | <0.005 | 0.0085 | 0.041 | 0.348 | 0.264 | 0.079 | <0.018 | 0.203 | <0.010 | <0.0125 | 0.00099 |
|  | FACILITY B AVERAGE | 0.0025 | 0.0190 | 0.0363 | 0.2647 | 0.2380 | 0.0617 | 0.0090 | 0.1693 | 0.0050 | 0.0050 | 0.0007 |
|  | STANDARD DEVIATION | 0.0000 | 0.0148 | 0.0119 | 0.1629 | 0.0440 | 0.0267 | 0.0000 | 0.0585 | 0.0000 | 0.0000 | 0.0004 |
| C | Unit 2, 9/28 | 0.214 | 0.0098 | 0.066 | 0.801 | 0.213 | 0.6 | 0.078 | 9.67 | <0.010 | <0.0125 | 0.00032 |
| C | Unit 2, 9/30 | 0.042 | 0.014 | 0.064 | 2 | 0.289 | 0.84 | 0.139 | 7.04 | <0.010 | <0.0125 | 0.00032 |
|  | FACILITY C AVERAGE | 0.1280 | 0.0119 | 0.0650 | 1.4005 | 0.2510 | 0.7200 | 0.1085 | 8.3550 | 0.0050 | 0.0050 | 0.0003 |
|  | STANDARD DEVIATION | 0.0860 | 0.0021 | 0.0010 | 0.5995 | 0.0380 | 0.1200 | 0.0305 | 1.3150 | 0.0000 | 0.0000 | 0.0000 |
| D | Unit 2, 10/3 | 0.795 | 0.408 | 2.51 | 35 | 19.1 | 7.47 | 0.19 | 64.6 | 0.202 | <0.0125 | 0.022 |
| D | Unit 2, 10/3, Dup | 1.3 | 0.646 | 3.86 | 56.2 | 27.8 | 12.6 | 0.322 | 132 | 0.267 | <0.0125 | 0.02 |
| D | Unit 2, 10/4 | 1.91 | 1.12 | 13.1 | 141 | 37.9 | 10.6 | 0.849 | 192 | 0.542 | <0.0125 | 0.0039 |
|  | FACILITY D AVERAGE | 1.3350 | 0.7247 | 6.4900 | 77.4000 | 28.2667 | 10.2233 | 0.4537 | 129.53 | 0.3370 | 0.0050 | 0.0153 |
|  | STANDARD DEVIATION | 0.4559 | 0.2959 | 4.7064 | 45.7972 | 7.6822 | 2.1112 | 0.2847 | 52.04 | 0.1474 | 0.0000 | 0.0081 |
|  | TOTAL NUMBER | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
|  | MINIMUM | 0.0025 | 0.0085 | 0.02 | 0.037 | 0.176 | 0.024 | 0.009 | 0.087 | 0.005 | 0.0125 | 0.0001 |
|  | MAXIMUM | 1.91 | 1.12 | 13.1 | 141 | 37.9 | 12.6 | 0.849 | 192 | 0.542 | 0.0125 | 0.022 |
|  | OVERALL AVERAGE | 0.4448 | 0.2286 | 2.008 | 23.88 | 9.603 | 3.257 | 0.1623 | 41.68 | 0.1058 | 0.0125 | 0.0072 |
|  | STANDARD DEVIATION | 0.6369 | 0.3631 | 3.906 | 43.10 | 13.054 | 4.712 | 0.2496 | 64.26 | 0.1716 | 0.0000 | 0.0086 |

## TABLE 4.11 TOTAL METALS DATA FOR FIELD WATER SAMPLES

### GROUNDWATER

| Facility | Sample Description | Cd (mg/L) | Cr (mg/L) | Cu (mg/L) | Fe (mg/L) | Pb (mg/L) | Mn (mg/L) | Ni (mg/L) | Zn (mg/L) | As (mg/L) | Se (mg/L) | Hg (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A | #1 | <0.005 | 0.0067 | 0.0086 | 2.89 | <0.050 | 0.107 | <0.018 | 0.029 | <0.010 | <0.005 | <0.0002 |
| B | #2 | 0.0081 | 0.0054 | 0.012 | 0.971 | <0.050 | 1.57 | <0.018 | 0.039 | <0.010 | <0.025 | <0.0002 |
| C | #3 | <0.010 | <0.005 | 0.0 | 1.52 | <0.050 | 0.051 | <0.015 | <0.003 | 0.013 | <0.025 | <0.0002 |
| C | #4 | <0.010 | <0.005 | 0.011 | 1.29 | <0.050 | 0.051 | <0.015 | 0.0056 | <0.010 | <0.005 | <0.0002 |
| C | #17 | <0.010 | <0.005 | 0.015 | 0.0025 | <0.050 | 0.03 | <0.015 | 0.0041 | <0.010 | <0.005 | <0.0002 |
| C | Production Well | <0.005 | <0.004 | 0.0045 | 0.0084 | <0.050 | 0.055 | <0.018 | 0.016 | <0.010 | <0.005 | <0.0002 |
|  | TOTAL NUMBER | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 |
|  | MINIMUM | 0.0025 | 0.002 | 0.0045 | 0.0025 | 0.025 | 0.03 | 0.0065 | 0.0015 | 0.005 | 0.0025 | 0.0001 |
|  | MAXIMUM | 0.0081 | 0.0067 | 0.015 | 2.89 | 0.025 | 1.57 | 0.009 | 0.039 | 0.013 | 0.0125 | 0.0001 |
|  | OVERALL AVERAGE | 0.0047 | 0.0036 | 0.0095 | 1.114 | 0.0250 | 0.3107 | 0.0081 | 0.0159 | 0.0063 | 0.0058 | 0.0001 |
|  | STANDARD DEVIATION | 0.0019 | 0.0018 | 0.0036 | 0.986 | 0.0000 | 0.5637 | 0.0010 | 0.0139 | 0.0030 | 0.0047 | 0.0000 |

concentrations of metals in the ground water were almost negligible, with only manganese and iron ever exceeding the 1 mg/L level. Mercury, lead, selenium, and nickel were not found in any ground water samples, and cadmium and arsenic were found in only one sample, each. Iron was the predominant metal detected, followed sequentially by manganese, zinc, copper, chromium, arsenic, and cadmium.

A review of the quench water data showed that the variabilities between shifts and/or units were very small, except for Facility D where they were substantially higher. This observation was expected since the quench water samples from Facility D contained much higher quantities of solids than the samples from the other facilities. The variability between facilities was relatively large. Facility D had the highest concentration of every metal in the quench water, while Facility B had the lowest concentrations for nine out of the eleven metals. Iron and zinc were the most concentrated metals in the quench water, followed closely by lead, while mercury was the least concentrated metal.

Upon comparing the analytical results of the field leachates, ground water, and quench water, the following observations were noted. First, the quench water contained the highest concentration of metals, followed by the field leachate and ground water, sequentially. Second, there did not appear to be any correlation between the field leachate and ground water data for any given facility. Third, the quench water and field leachate results from Facility B are comparable, while the quench water metals concentrations from Facility D are an order of magnitude higher than the field leachate results. No similar trends for Facility C were observed. Finally, although Facility B had the lowest metals concentrations in its quench water and field leachate, it had the highest concentrations in its ground water (no background metals data was available for comparison).

### 4.4.2 Polychlorinated Biphenyls

The field leachates, quench water, and ground water samples were analyzed for individual PCB homologs and total PCBs. The results of these analyses are summarized by sample matrix and facility and are presented in Table 4.12. A review of this table shows that only negligible concentrations of PCBs were detected, with the highest total PCB concentration for any sample being only 0.03 ug/L. Additionally, only the three lowest chlorinated classes of PCBs (i.e., mono-, di-, and tri-) were detected.

### 4.4.3 Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzo-furans

The field leachate and quench water samples were analyzed for PCDDs and PCDFs in the tetra- through octa-chlorinated classes. Additionally, the 2,3,7,8-TCDD and 2,3,7,8-TCDF isomers were identified and quantified. The results of these analyses are summarized by sample matrix and facility in Table 4.13.

A review of the PCDD homolog concentrations in the field leachates showed that the variabilities between samples at a given facility and between facilities were both extremely high (i.e., the standard deviations of the results exceeded the averages). Because the field leachate samples at a given facility were collected within 100 to 200 feet of each other, this variability between samples at a given facility was not anticipated. Two possible explanations for these observed differences are (1) some of the samples appeared to be natural seeps (i.e., "true" field leachate) that were turbid and expected to contain more leachable constituents than the other samples, which appeared to be surface water runoff, and (2) the heterogeneity of the disposed ash materials may have caused "pockets" or areas of more highly contaminated ash located in random areas of the landfill. The leachates from Facility C contained the highest concentrations of PCDDs, and the leachates from Facilities B and D had approximately equal PCDD concentrations which were less than those from Facility C. The hepta-CDD homolog was the most abundant, and the tetra-CDD homolog was the least abundant. The 2,3,7,8-TCDD isomer accounted for 6 percent of the tetra-CDD homologs and 0.4 percent of the total PCDDs.

## TABLE 4.12 PCBs IN FIELD WATER SAMPLES

### FIELD LEACHATE

| Plant | Sample Description | MONO -CB ug/L | DI -CB ug/L | TRI -CB ug/L | TETRA -CB ug/L | PENTA -CB ug/L | TOTAL PCB ug/L |
|---|---|---|---|---|---|---|---|
| B | East Side | | | | | | 0 |
| B | North Side | | | | | | 0 |
| B | Northeast Corner | | | | | | 0 |
| C | North Side | | 0.002 | | | | 0.002 |
| C | Northeast Corner | | | | | | 0 |
| C | Northwest Corner | | | | | | 0 |
| D | Northeast Corner | | | | | | 0 |
| D | Northeast Corner, Dup | | | | | | 0 |
| D | Southeast Corner | | | 0.008 | | | 0.008 |
| | NUMBER OF PCBs FOUND | 0 | 1 | 1 | 0 | 0 | 2 |

### GROUNDWATER

| Plant | Sample Description | MONO -CB ug/L | DI -CB ug/L | TRI -CB ug/L | TETRA -CB ug/L | PENTA -CB ug/L | TOTAL PCB ug/L |
|---|---|---|---|---|---|---|---|
| C | #17 | | | | | | 0 |
| C | #3 | | | | | | 0 |
| C | #4 | | | | | | 0 |
| C | Production Well | | | | | | 0 |
| | NUMBER OF PCBs FOUND | 0 | 0 | 0 | 0 | 0 | 0 |

## TABLE 4.12 PCBs IN FIELD WATER SAMPLES

### QUENCH WATER

| Plant | Sample Description | MONO -CB ug/L | DI -CB ug/L | TRI -CB ug/L | TETRA -CB ug/L | PENTA -CB ug/L | TOTAL PCB ug/L |
|---|---|---|---|---|---|---|---|
| A | Unit 1, 9/26 | | | | | | 0 |
| A | Unit 2, 9/26 | | 0.004 | | | | 0.004 |
| B | Unit 3, 9/28 | | | | | | 0 |
| B | Unit 4, 9/28 | | | | | | 0 |
| B | Unit 4, 9/28, Dup | 0.03 | | | | | 0.03 |
| C | Unit 2, 9/28 | | | | | | 0 |
| C | Unit 2, 9/30 | 0.02 | | | | | 0.02 |
| D | Unit 2, 10/3 | | | | | | 0 |
| D | Unit 2, 10/3, Dup | | | | | | 0 |
| D | Unit 2, 10/4 | | | | | | 0 |
| | NUMBER OF PCBs FOUND | 2 | 1 | 0 | 0 | 0 | 3 |

## TABLE 4.13 PCDO AND PCDF IN FIELD WATER SAMPLES

### FIELD LEACHATE (DIOXIN HOMOLOGS)

| Plant | Sample Description | 2,3,7,8 TCDD (ng/l) | TETRA -CDD (ng/l) | PENTA -CDD (ng/l) | HEXA -CDD (ng/l) | HEPTA -CDD (ng/l) | OCTA -CDD (ng/l) | TOTAL -CDD (ng/l) |
|---|---|---|---|---|---|---|---|---|
| B | East Side | <0.06 | <0.06 | <0.05 | <0.02 | 0.009 | 0.14 | 0.149 |
| B | North Side | <0.48 | <0.48 | 0.75 | 1.7 | 2.4 | 1.6 | 6.45 |
| B | Northeast Corner | 0.28 | 6.6 | 25 | 22 | 21 | 14 | 88.6 |
| C | North Side | <0.22 | <0.22 | <0.04 | 2 | 2.6 | 1.9 | 6.5 |
| C | Northeast Corner | 1.6 | 28 | 93 | 130 | 172 | 120 | 543 |
| C | Northwest Corner | <0.05 | <0.05 | <0.03 | <0.02 | <0.02 | 0.06 | 0.06 |
| D | Northeast Corner | <0.22 | 0.13 | 0.4 | 2.2 | 8.2 | 23 | 33.93 |
| D | Northeast Corner, Dup | <0.26 | 0.27 | <0.22 | 2.1 | 8.8 | 25 | 36.17 |
| D | Southeast Corner | | | | | | | |
| | TOTAL NUMBER | 8 | 8 | 8 | 8 | 8 | 8 | 8 |
| | MINIMUM | 0.025 | 0.025 | 0.015 | 0.01 | 0.009 | 0.06 | 0.06 |
| | MAXIMUM | 1.6 | 28 | 93 | 130 | 172 | 120 | 543 |
| | OVERALL AVERAGE | 0.32 | 4.43 | 14.9 | 20.0 | 26.9 | 23.2 | 89.4 |
| | STANDARD DEVIATION | 0.49 | 9.16 | 30.6 | 42.1 | 55.2 | 37.8 | 173.7 |

### FIELD LEACHATE (FURAN HOMOLOGS)

| Plant | Sample Description | 2,3,7,8 TCDF (ng/l) | TETRA -CDF (ng/l) | PENTA -CDF (ng/l) | HEXA -CDF (ng/l) | HEPTA -CDF (ng/l) | OCTA -CDF (ng/l) | TOTAL -CDF (ng/l) | TCDD + TCDF (ng/l) |
|---|---|---|---|---|---|---|---|---|---|
| B | East Side | <0.05 | <0.05 | <0.02 | <0.01 | 0.05 | 0.05 | 0.1 | 0.249 |
| B | North Side | 0.3 | 0.95 | 1.1 | 0.83 | 0.85 | 0.35 | 4.08 | 10.53 |
| B | Northeast Corner | 3.7 | 22 | 17 | 16 | 9.4 | 1.9 | 66.3 | 154.9 |
| C | North Side | <0.22 | <0.22 | 0.89 | 1.2 | 0.89 | 0.32 | 3.3 | 9.8 |
| C | Northeast Corner | 11 | 65 | 64 | 76 | 60 | 15 | 280 | 823 |
| C | Northwest Corner | <0.08 | <0.08 | <0.02 | <0.01 | <0.03 | 0.04 | 0.04 | 0.1 |
| D | Northeast Corner | 0.37 | 3 | 2.3 | 1.9 | 1.3 | 0.84 | 9.34 | 43.27 |
| D | Northeast Corner, Dup | 0.4 | 2.9 | 2.4 | 1.9 | 1.2 | 0.81 | 9.21 | 45.38 |
| D | Southeast Corner | | | | | | | | |
| | TOTAL NUMBER | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 |
| | MINIMUM | 0.025 | 0.025 | 0.01 | 0.005 | 0.015 | 0.04 | 0.04 | 0.1 |
| | MAXIMUM | 11 | 65 | 64 | 76 | 60 | 15 | 280 | 823 |
| | OVERALL AVERAGE | 1.99 | 11.8 | 11.0 | 12.2 | 9.2 | 2.4 | 46.5 | 136 |
| | STANDARD DEVIATION | 3.59 | 21.3 | 20.7 | 24.6 | 19.4 | 4.8 | 90.6 | 264 |

## TABLE 4.13 PCDD AND PCDF IN FIELD WATER SAMPLES

### QUENCH WATER (DIOXIN HOMOLOGS)

| Plant | Sample Description | 2,3,7,8 TCDD (ng/l) | TETRA -CDD (ng/l) | PENTA -CDD (ng/l) | HEXA -CDD (ng/l) | HEPTA -CDD (ng/l) | OCTA -CDD (ng/l) | TOTAL -CDD (ng/l) |
|---|---|---|---|---|---|---|---|---|
| A | Unit 1, 9/26 | <0.08 | 0.1 | 0.82 | 0.66 | 0.58 | 0.43 | 2.59 |
| A | Unit 2, 9/26 | <0.08 | 2 | 4 | 2 | 1.9 | 0.98 | 10.88 |
| B | Unit 4, 9/28 | <0.07 | <0.07 | <0.03 | <0.01 | <0.03 | 0.06 | 0.06 |
| B | Unit 4, 9/28, Dup | <0.07 | <0.07 | <0.05 | <0.04 | 0.05 | 0.13 | 0.18 |
| C | Unit 2, 9/28 | <0.17 | <0.17 | 0.26 | 1.1 | 1.5 | 1.2 | 4.06 |
| C | Unit 2, 9/30 | <0.81 | 0.59 | 5.9 | 10 | 19 | 12 | 47.49 |
| D | Unit 2, 10/3 | 8.2 | 190 | 610 | 500 | 450 | 250 | 2000 |
| D | Unit 2, 10/3, Dup | 17 | 700 | 650 | 450 | 420 | 330 | 2550 |
| D | Unit 2, 10/4 | 1 | 24 | 80 | 72 | 77 | 53 | 306 |
|  | TOTAL NUMBER | 9 | 9 | 9 | 9 | 9 | 9 | 9 |
|  | MINIMUM | 0.035 | 0.035 | 0.015 | 0.005 | 0.015 | 0.06 | 0.06 |
|  | MAXIMUM | 17 | 700 | 650 | 500 | 450 | 330 | 2550 |
|  | OVERALL AVERAGE | 2.98 | 102 | 150 | 115 | 108 | 72 | 547 |
|  | STANDARD DEVIATION | 5.55 | 219 | 258 | 194 | 177 | 119 | 937 |

### QUENCH WATER (FURAN HOMOLOGS)

| Plant | Sample Description | 2,3,7,8 TCDF (ng/l) | TETRA -CDF (ng/l) | PENTA -CDF (ng/l) | HEXA -CDF (ng/l) | HEPTA -CDF (ng/l) | OCTA -CDF (ng/l) | TOTAL -CDF (ng/l) | TCDD + TCDF (ng/l) |
|---|---|---|---|---|---|---|---|---|---|
| A | Unit 1, 9/26 | 0.27 | 1.7 | 0.91 | 0.51 | 0.36 | 0.27 | 4.02 | 6.61 |
| A | Unit 2, 9/26 | 2.1 | 12 | 6.1 | 3.1 | 1.2 | 0.27 | 24.77 | 35.65 |
| B | Unit 4, 9/28 | <0.06 | <0.06 | <0.01 | <0.01 | <0.02 | <0.15 | 0 | 0.06 |
| B | Unit 4, 9/28, Dup | <0.08 | <0.08 | <0.04 | <0.02 | 0.04 | <0.30 | 0.04 | 0.22 |
| C | Unit 2, 9/28 | 0.14 | 0.98 | 0.76 | 0.61 | 0.52 | 0.25 | 3.12 | 7.18 |
| C | Unit 2, 9/30 | 0.55 | 2.4 | 4 | 6.2 | 6.5 | 1.4 | 20.5 | 67.99 |
| D | Unit 2, 10/3 | 110 | 640 | 560 | 490 | 310 | 75 | 2075 | 4075 |
| D | Unit 2, 10/3, Dup | 99 | 590 | 460 | 390 | 280 | 68 | 1788 | 4338 |
| D | Unit 2, 10/4 | 14 | 91 | 83 | 81 | 59 | 16 | 330 | 636 |
|  | TOTAL NUMBER | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 |
|  | MINIMUM | 0.03 | 0.03 | 0.005 | 0.005 | 0.01 | 0.075 | 0 | 0.06 |
|  | MAXIMUM | 110 | 640 | 560 | 490 | 310 | 75 | 2075 | 4338 |
|  | OVERALL AVERAGE | 25.1 | 149 | 124 | 108 | 73 | 18 | 472 | 1019 |
|  | STANDARD DEVIATION | 42.7 | 251 | 209 | 181 | 120 | 29 | 790 | 1716 |

The PCDF homolog concentrations in the field leachates again showed that the variabilities between samples at a given facility and between facilities were both extremely high. The leachates from Facility C contained the highest PCDF concentrations, followed by the leachates from Facilities B and D, sequentially. The concentrations of the tetra-, penta-, and hexa-CDF homologs were approximately equal, and these three homologs were the most abundant. The octa-CDF homolog was the least abundant. The 2,3,7,8-TCDF isomer accounted for 15 percent of the total tetra-CDFs and 5 percent of the total PCDFs.

Upon comparing the results of the PCDDs with the PCDFs in the field leachate samples, the following observations were noted. First, the leachates from Facility C contained the highest concentrations of both PCDDs and PCDFs, and the leachates from Facilities B and D contained approximately equal concentrations of both PCDDs and PCDFs. Second, the abundances of the tetra-CDD and tetra-CDF homologs appeared to be inversely proportional (i.e., the least abundant PCDD homolog and the most abundant PCDF homolog). Third, the abundances of the octa-CDD and octa-CDF homologs also showed this inverse proportionality. Finally, there did not appear to be any correlation between the relative abundances of PCDDs or PCDFs in the total PCDD/PCDF concentrations.

The PCDD results for the quench water showed that the variability between shifts and units was relatively small compared to the variability between facilities. This suggests that the different combustion conditions and feed materials at each facility contribute to this variability. The quench water samples from Facility D contained the highest PCDD concentrations, followed by the quench water samples from Facilities C and B, sequentially. There did not appear to be any correlations for the least or most abundant homologs, or for the 2,3,7,8-TCDD isomer.

A review of the PCDF concentrations in the quench water again showed that the variability between shifts and units was relatively small compared to the variability between facilities. The quench water from

Facility D contained the highest PCDF concentrations, followed by the quench water samples from Facilities C and B, sequentially. Again, there did not appear to be any trends for the least or most abundant homologs, or for the 2,3,7,8-TCDF isomer.

For quench water, comparing the PCDD results with the PCDF results indicated the total concentrations of PCDDs and PCDFs followed the same sequence of abundance by homolog among the facilities. However, there were no correlations for the individual homologs, or for the relative abundances of PCDDs or PCDFs in the PCDD/PCDF total concentrations.

Upon comparing the field leachate results with the results from the quench water samples, the following observation was noted. The field leachate samples from Facilities B and C contained more PCDDs and PCDFs than the quench water samples from the facilities. However, the quench water samples from Facility D contained 10 times more PCDDs and PCDFs than the field leachate samples from this facility. This suggests that the PCDDs and PCDFs at Facility D are readily leached from the solid ash material in the quench water tank. Conversely, at Facilities B and C the PCDDs and PCDFs appear to leach more slowly until the ash is disposed in the landfill.

### 4.4.4 Organic Constituents

The field leachates, quench water, and ground water samples were analyzed for organic constituents, including: TOC, organic scan, and BNAs. The results of these analyzes are summarized by sample matrix and facility in Table 4.14.

A review of the field leachate data showed that Facility D, had the highest TOC and BNA constituent concentrations. Similarly, Facility B had the lowest TOC and BNA constituent concentrations. The predominant BNAs were thiolane, ethylhexyl phthalate, and dimethylpropanediol.

A review of the quench water data showed that the variabilities between units and facilities were relatively large. Facility D had the highest concentrations of TOC and BNA constituents, followed sequentially

## TABLE 4.14 ORGANIC CONSTITUENTS IN FIELD WATER SAMPLES

**FIELD LEACHATES**

| Plant | Sample Description | TOC (mg/l) | Organic Scan (mg/l) | BNA Peaks Found (No.) | Ethyl Hexyl Phthalate 117817 (ug/L) | Dimethyl Propane Diol 126307 (ug/L) | Biphenyl 90437 (ug/L) | Hexa Thiepane 17233715 (ug/L) | Thiolane 289167 (ug/L) |
|---|---|---|---|---|---|---|---|---|---|
| B | East Side | 189.0 | <0.25 | 2 | | | | | |
| B | Northeast Corner | 204.0 | <0.25 | 3 | | 9 | | | |
| B | North Side | 273.0 | <0.25 | 4 | | 22 | | | |
| C | Northwest Corner | 379.0 | <0.25 | 2 | | | | | |
| C | Northeast Corner | 187.0 | 2.5 | 8 | 12 | | | | |
| C | North Side | 59.1 | <0.25 | 1 | | | | | |
| D | Southeast Corner | 574.0 | <0.25 | 21 | 7 | | | | |
| D | Northeast Corner | 636.0 | <0.25 | 22 | 80 | 110 | 51 | 82 | 400 |
| D | Northeast Corner, Dup | 567.0 | | 24 | 37 | 120 | 51 | | 140 |
| | No. | 9 | 8 | 9 | 4 | 4 | 2 | 1 | 2 |
| | Min. | 59.1 | 0 | 1 | 7 | 9 | 51 | 82 | 140 |
| | Max. | 636 | 2.5 | 24 | 80 | 120 | 51 | 82 | 400 |
| | Avg. | 340.9 | NA | 9.7 | 34.0 | 65.3 | 51.0 | 82.0 | 270.0 |
| | Std. Dev. | 195.4 | NA | 9.2 | 28.9 | 50.1 | 0.0 | 0.0 | 130.0 |

| Plant | Sample Description | Benz-aldehyde 100527 (ug/L) | Sulfo-nylbis Sulfur 67710 (ug/L) | Unknown HCs (#) | Unknowns (#) |
|---|---|---|---|---|---|
| B | East Side | | | | 2 |
| B | Northeast Corner | | | | 2 |
| B | North Side | | | | 3 |
| C | Northwest Corner | | 11 | | 1 |
| C | Northeast Corner | 8 | | 2 | 4 |
| C | North Side | | | | 1 |
| D | Southeast Corner | | | 4 | 16 |
| D | Northeast Corner | | | 9 | 8 |
| D | Northeast Corner, Dup | | | 10 | 10 |
| | No. | 1 | 1 | | |
| | Min. | 8 | 11 | | |
| | Max. | 8 | 11 | | |
| | Avg. | 8.0 | 11.0 | | |
| | Std. Dev. | 0.0 | 0.0 | | |

## TABLE 4.14 ORGANIC CONSTITUENTS IN FIELD WATER SAMPLES

QUENCH WATER

| Plant | Sample Description | TOC (mg/l) | Organic Scan (mg/l) | BNA Peaks Found (No.) | Phenol 108952 (ug/L) | 2-Methyl phenol 95487 (ug/L) | 4-Methyl phenol 106445 (ug/L) | Dimethyl phenol 105679 (ug/L) | Benzoic Acid 65850 (ug/L) | Naphthalene 91203 (ug/L) |
|---|---|---|---|---|---|---|---|---|---|---|
| A | Unit 2, 9/26 | 94.5 | <0.25 | 29 | 65 | 6 | | | 36 | 8 |
| A | Unit 1, 9/26 | 26.9 | <0.25 | 8 | | | | | 260 | |
| B | Unit 3, 9/28 | 77.3 | <0.25 | 23 | 170 | 17 | | | 300 | |
| B | Unit 4, 9/28, Dup | 421.0 | <0.25 | 20 | 380 | 40 | 92 | | 2100 | |
| B | Unit 4, 9/28 | 416.5 | <0.25 | 20 | 380 | 44 | 94 | | 2100 | |
| C | Unit 2, 9/28 | 3.2 | 12.3 | | | | | | | |
| C | Unit 2, 9/30 | 29.2 | <0.25 | 5 | | | | | | |
| D | Unit 2, 10/3 | 165.0 | <0.25 | 25 | 60 | 7 | 23 | | 570 | |
| D | Unit 2, 10/3, Dup | 153.0 | | 25 | 71 | 7 | | | 900 | |
| D | Unit 2, 10/4 | 1228.0 | <0.25 | 25 | 640 | 86 | | 44 | 3800 | |
| | No. | 10 | 9 | 9 | 7 | 7 | 3 | 1 | 8 | 1 |
| | Min. | 3.2 | 0.125 | 5 | 60 | 6 | 23 | 44 | 36 | 8 |
| | Max. | 1228 | 12.3 | 29 | 640 | 86 | 94 | 44 | 3800 | 8 |
| | Avg. | 261.5 | 1.48 | 20.0 | 252.3 | 29.6 | 69.7 | 44.0 | 1258.3 | 8.0 |
| | Std. Dev. | 352.4 | 3.83 | 7.7 | 205.2 | 27.3 | 33.0 | 0.0 | 1219.0 | 0.0 |

| Plant | Sample Description | Acenaphthylene 208968 (ug/L) | Phenanthrene 85018 (ug/L) | Butyl Phthalate 84742 (ug/L) | Fluoranthene 206440 (ug/L) | Pyrene 129000 (ug/L) | Ethyl Hexyl Phthalate 117817 (ug/L) | Methyl Butanoic Acid 116530 (ug/L) | Molecular Sulfur 10544500 (ug/L) | Thiolane 289167 (ug/L) |
|---|---|---|---|---|---|---|---|---|---|---|
| A | Unit 2, 9/26 | 6 | 6 | | 6 | 5 | | | | |
| A | Unit 1, 9/26 | | | | | | | | | |
| B | Unit 3, 9/28 | | | 3 | | | | | | |
| B | Unit 4, 9/28, Dup | | | | | | | | 29 | |
| B | Unit 4, 9/28 | | | | | | | | 130 | 23 |
| C | Unit 2, 9/28 | | | | | | | | | |
| C | Unit 2, 9/30 | | | | | | | 33 | | |
| D | Unit 2, 10/3 | | | | | | 8 | | | |
| D | Unit 2, 10/3, Dup | | | | | | | | | |
| D | Unit 2, 10/4 | | | | | | | | | |
| | No. | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 2 | 1 |
| | Min. | 6 | 6 | 3 | 6 | 5 | 8 | 33 | 29 | 23 |
| | Max. | 6 | 6 | 3 | 6 | 5 | 8 | 33 | 130 | 23 |
| | Avg. | 6.0 | 6.0 | 3.0 | 6.0 | 5.0 | 8.0 | 33.0 | 79.5 | 23.0 |
| | Std. Dev. | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 50.5 | 0.0 |

## TABLE 4.14 ORGANIC CONSTITUENTS IN FIELD WATER SAMPLES

| Plant | QUENCH WATER<br>============<br>Sample Description | 2-Hydrox Benzoic Acid 69727 (ug/L) | Hydroxy Methyl Pentenone 80717 (ug/L) | Pyran Naphtho Dione 81845 (ug/L) | Hydroxy Methyl Pyranone 118718 (ug/L) | Hydro Pyranone 542280 (ug/L) | Hexanoic Acid 142621 (ug/L) | Methyl Pentanoic Acid 646071 (ug/L) | Benz-aldehyde 100527 (ug/L) | Methyl Pentane-diol 144194 (ug/L) |
|---|---|---|---|---|---|---|---|---|---|---|
| A | Unit 2, 9/26 | | | 6 | 11 | 11 | 22 | | | |
| A | Unit 1, 9/26 | | | | | | 10 | | | |
| B | Unit 3, 9/28 | 40 | 26 | | | | 30 | | | |
| B | Unit 4, 9/28, Dup | 50 | | | | | 58 | | | |
| B | Unit 4, 9/28 | 42 | | | | | 37 | | | |
| C | Unit 2, 9/28 | | | | | | | | | |
| C | Unit 2, 9/30 | | | | | | | | | |
| D | Unit 2, 10/3 | | | | | | 45 | 17 | 22 | 17 |
| D | Unit 2, 10/3, Dup | | | | | | 51 | 84 | | |
| D | Unit 2, 10/4 | | | | 130 | | 920 | 88 | | |
| | No. | 3 | 1 | 1 | 2 | 1 | 8 | 3 | 1 | 1 |
| | Min. | 40 | 26 | 6 | 11 | 11 | 10 | 17 | 22 | 17 |
| | Max. | 50 | 26 | 6 | 130 | 11 | 920 | 88 | 22 | 17 |
| | Avg. | 44.0 | 26.0 | 6.0 | 70.5 | 11.0 | 146.6 | 63.0 | 22.0 | 17.0 |
| | Std. Dev. | 4.3 | 0.0 | 0.0 | 59.5 | 0.0 | 292.7 | 32.6 | 0.0 | 0.0 |

| Plant | Sample Description | Furan Carbox-aldehyde 67470 (ug/L) | Benzene Propanoic Acid 501520 (ug/L) | Tetra Decanoic Acid 544638 (ug/L) | Methyl Purine Dione 58082 (ug/L) | Benzene Acetic Acid 103822 (ug/L) | Decanoic Acid 334485 (ug/L) | Unknown Org Acids (#) | Unknown HCs (#) | Unknowns (#) |
|---|---|---|---|---|---|---|---|---|---|---|
| A | Unit 2, 9/26 | | | | | | | 2 | | 15 |
| A | Unit 1, 9/26 | | | | | | | | | 6 |
| B | Unit 3, 9/28 | | | | | | | | | 16 |
| B | Unit 4, 9/28, Dup | | | | | | | | | 13 |
| B | Unit 4, 9/28 | | | | | | | | | 12 |
| C | Unit 2, 9/28 | | | | | | | | | |
| C | Unit 2, 9/30 | | | | | | | | | 4 |
| D | Unit 2, 10/3 | 54 | 23 | 72 | 23 | | | 1 | 2 | 9 |
| D | Unit 2, 10/3, Dup | | 12 | | 22 | | | 1 | | 17 |
| D | Unit 2, 10/4 | | | | | 120 | 160 | 2 | 1 | 13 |
| | No. | 1 | 2 | 1 | 2 | 1 | 1 | | | |
| | Min. | 54 | 12 | 72 | 22 | 120 | 160 | | | |
| | Max. | 54 | 23 | 72 | 23 | 120 | 160 | | | |
| | Avg. | 54.0 | 17.5 | 72.0 | 22.5 | 120.0 | 160.0 | | | |
| | Std. Dev. | 0.0 | 5.5 | 0.0 | 0.5 | 0.0 | 0.0 | | | |

## TABLE 4.14 ORGANIC CONSTITUENTS IN FIELD WATER SAMPLES

**GROUNDWATER**

| Plant | Sample Description | TOC (mg/l) | Organic Scan (mg/l) | BNA Peaks Found (No.) | Ethyl Hexyl Phthalate 117817 (ug/L) | Unknowns (#) |
|---|---|---|---|---|---|---|
| A | #1 | 3.4 | <0.25 | | | |
| B | #2 | 2.7 | <0.25 | | | |
| C | #3 | 80.9 | <0.25 | 0 | | |
| C | #17 | 76.1 | <0.25 | 2 | 9 | 1 |
| C | #4 | 97.4 | <0.25 | 0 | | |
| C | Production Well | 2.0 | <0.25 | | | |
| | No. | 6 | | | | |
| | Min. | 2 | | | | |
| | Max. | 97.4 | | | | |
| | Avg. | 43.75 | | | | |
| | Std. | 41.56 | | | | |

NOTE:

Names of organic constituents abbreviated;
CAS numbers provided with constituent names

by Facilities B, A, and C. The predominant BNAs detected were benzoic acid, phenol, hexanoic acid, benzene acetic acid, and decanoic acid.

A review of the ground water data showed that the variability of the TOC data between facilities was relatively high. Facility C had the highest TOC concentrations, with Facilities A and B having approximately equal concentrations significantly less than Facility C. Only one ground water sample contained detectable quantities of BNA constituents - Well 17 at Facility C. The only BNA positively identified was bis-ethylhexyl phthalate.

Upon comparing the results from the different sample matrices, the following observations were noted. First, the quench water contained the highest quantities of BNA constituents, and the second highest quantity of TOC. The field leachates contained the highest concentrations of TOC and the second highest of BNA constituents. Second, there appeared to be a slight correlation between TOC and BNA concentrations, however, there did not appear to be any relationship between TOC or BNA and organic scan. Finally, it was observed that certain BNA compounds were always detected together. Phenol, methylphenol (phenolic derivatives), benzoic acid, and hexanoic acid (carboxylic acids) were always found together, as were naphthalene, acenaphthylene, phenanthrene, fluoranthene, and pyrene (polycyclic aromatic hydrocarbons).

### 4.5 Quality Assurance/Quality Control Summary

The Versar laboratory and Versar's subcontract laboratory, Battelle Columbus, which conducted analyses for PCDDs and PCDFs, implemented extensive quality control measures on all analyses. The procedures used by the Versar laboratory conformed to the EPA Contract Laboratory Program requirements. During all analytical activities, quality control (QC) samples were introduced into the sampling scheme in order to evaluate the precision and accuracy of the analytical method. These QC samples included laboratory-prepared QC samples (e.g., reagent blanks, duplicates, matrix spikes, surrogate spikes, and check standards) and "blind" field duplicates (at a frequency of 25 percent per sampling plan specifications), trip blanks, and field blanks. The field duplicate samples were indicative of the precision of the entire sampling and analysis method. The results of the QA/QC analyses are summarized in the following subsections by major categories of analyses--total metals, PCBs, PCDD/PCDFs, and organic constituents. The original data reports from the laboratories provide more extensive QC data and are included in the appendices of this report. All data quality objectives and control procedures were described in a QA Plan which was submitted to EPA for review and approved prior to the initiation of chemical analysis.

### 4.5.1 Internal QA/QC

The internal QA/QC samples were prepared in the laboratory as required by the analytical method to evaluate the performance of the method. The following sections present the results and evaluations of the internal QA/QC samples for metals, PCBs, PCDD/PCDFs, and organic constituents.

4.5.1.1 Total Metals Analyses - Analyses of solid residues, field water samples, and laboratory-prepared leachates for total metals were performed by the Versar laboratory. Analyses of each sample batch for each matrix (solid, field water, laboratory leachates) were accompanied by internal QC checks consisting of the following analyses: reference standard, calibration blank, one or two reagent blanks, a check standard different from the reference standard, one sample duplicate selected at random from the batch, and one spike. The standards were used to check on the accuracy of calibration, the blanks are used to identify contamination in reagents and laboratory water, the duplicates indicate the precision or reproducibility of the analyses as the Relative Percent Difference (RPD), and the spikes indicate the accuracy of analyses in terms of the capabilities of the analyses to measure the constituent, or percent recovery of any added spike.

The results of these internal QC checks for total metal analyses are summarized in Table 4.15. The QC criteria for total metals analyses in

## TABLE 4.15 QC SUMMARY (INTERNAL) FOR METALS

| Fly Ash and Bottom Ash Digestates | UNITS | ICP ANALYSES | | | | | | | | AA ANALYSES | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Cd | Cr | Cu | Fe | Pb | Mn | Ni | Zn | As | Se | Hg |
| Reference Standard | % Recovered | 97.1 | 97.4 | 98.0 | 103.1 | 101.6 | 95.7 | 92.9 | 97.7 | 100.0 | 89.6 | 93.2 |
| Calibration Blank | ug/L | <10 | <5 | <5 | <4 | <50 | <2 | <15 | <3 | <10 | <5 | <0.2 |
| Reagent Blank 1 | ug/L | <10 | <5 | <5 | 13 | <50 | 2.1 | <15 | 4.2 | <10 | <5 | <0.2 |
| Reagent Blank 2 | ug/L | <10 | <5 | <5 | 20 | <50 | <2 | <15 | 9.5 | | | |
| Check Standard | % Recovered | 95.7 | 91.7 | 92.5 | 97.4 | 93.8 | 91.4 | 95.3 | 95.0 | 114.0 | 88.0 | 108.0 |
| Sample Duplicate (Sample 17667) | %RPD | 4.3 | 0.0 | 5.2 | 15.1 | 4.4 | 4.6 | 1.4 | 3.9 | 18.0 | 8.3 | (1) |
| Spike Recovery | % Recovered | (2) | 20.0 | (2) | (2) | (2) | (2) | (2) | (2) | (2) | 50.0 | 98.0 |

| Field Water Samples Batches 1-4 (Ground Water & Quench) | UNITS | ICP ANALYSES | | | | | | | | AA ANALYSES | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Cd | Cr | Cu | Fe | Pb | Mn | Ni | Zn | As | Se | Hg |
| Reference Standard | % Recovered | 98.6 | 94.4 | 95.5 | 95.5 | 98.6 | 95.0 | 96.0 | 99.5 | 104.3 | 87.6 | 102.3 |
| Calibration Blank | ug/L | <10 | <5 | <5 | <4 | <50 | <2 | <15 | <3 | <10 | <5 | <0.2 |
| Reagent Blank 1 | ug/L | <10 | 8.9 | 5.5 | 27 | <50 | 19 | <15 | 9.3 | <10 | <5 | <0.2 |
| Check Standard | % Recovered | 101.7 | 98.0 | 100.0 | 98.5 | 98.4 | 98.5 | 102.0 | 104.5 | 91.0 | 100.0 | 88.0 |
| Sample Duplicate (Sample 19582) | %RPD | 0.0 | (1) | 1.1 | 67.7 | (1) | 5.6 | (1) | 13.3 | (1) | (1) | (1) |
| Spike Recovery | % Recovered | 82.0 | 85.1 | 89.0 | 86.8 | 79.5 | 91.5 | 83.5 | 86.0 | 104.0 | 86.0 | 115.0 |

| Field Water Samples Batches 5 (GW & Field Leachates) | UNITS | ICP ANALYSES | | | | | | | | AA ANALYSES | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Cd | Cr | Cu | Fe | Pb | Mn | Ni | Zn | As | Se | Hg |
| Reference Standard | % Recovered | 98.2 | 94.8 | 93.5 | 93.5 | 103.6 | 94.0 | 95.0 | 99.5 | 106.5 | 85.7 | 97.7 |
| Calibration Blank | ug/L | <10 | <5 | <5 | <5 | <50 | <1 | <15 | 13 | <10 | <5 | <0.2 |
| Reagent Blank 1 | ug/L | <10 | <5 | 44 | 21 | <50 | <1 | <15 | 22 | <10 | <5 | <0.2 |
| Check Standard | % Recovered | 100.5 | 102.8 | 93.0 | 101.5 | 106.5 | 101.5 | 100.5 | 105.0 | 82.0 | 98.0 | 108.0 |
| Sample Duplicate (Sample 19765) | %RPD | (1) | (1) | 12.6 | 3.8 | (1) | 3.8 | (1) | 35.8 | (1) | (1) | (1) |
| Spike Recovery | % Recovered | 82.5 | 83.5 | 85.5 | 110.0 | 70.0 | 86.0 | 85.5 | 84.7 | 108.0 | 78.0 | 110.0 |

## TABLE 4.15 QC SUMMARY (INTERNAL) FOR METALS

| Field Water Samples Batches 6 (Field Leachates) | UNITS | ICP ANALYSES | | | | | | | | AA ANALYSES | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Cd | Cr | Cu | Fe | Pb | Mn | Ni | Zn | As | Se | Hg |
| Reference Standard | % Recovered | 97.4 | 96.8 | 100.0 | 98.0 | 108.1 | 98.5 | 106.0 | 100.5 | 115.2 | 87.6 | 97.7 |
| Calibration Blank | ug/L | <10 | <5 | <5 | <5 | <50 | <1 | <15 | <3 | <10 | <5 | <0.2 |
| Reagent Blank 1 | ug/L | <10 | <5 | <5 | 47 | <50 | 1.6 | <15 | 12 | <10 | <5 | <0.2 |
| Check Standard | % Recovered | 104.1 | 98.8 | 95.0 | 96.5 | 108.5 | 98.5 | 99.5 | 103.0 | 94.0 | 102.0 | 100.0 |
| Sample Duplicate (Sample 19831) | %RPD | (1) | (1) | 28.6 | 1.4 | (1) | 45.6 | (1) | 18.2 | (1) | (1) | (1) |
| Spike Recovery | % Recovered | 84.5 | 95.5 | 70.0 | 81.5 | 67.5 | 83.0 | 126.0 | 93.0 | 86.0 | 94.0 | 75.0 |

| EP Toxicity Leachates | UNITS | ICP ANALYSES | | | | | | | | AA ANALYSES | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Cd | Cr | Cu | Fe | Pb | Mn | Ni | Zn | As | Se | Hg |
| Reference Standard | % Recovered | 94.3 | 93.3 | 94.0 | 93.0 | 98.0 | 94.0 | 90.0 | 97.5 | 106.5 | 89.6 | 95.5 |
| Calibration Blank | ug/L | <10 | <5 | <5 | <5 | <50 | <1 | <15 | <3 | <10 | <5 | <2 |
| Reagent Blank 1 | ug/L | <10 | <5 | 11 | 19 | <50 | 2.3 | <15 | 116 | <10 | <5 | <2 |
| Check Standard | % Recovered | 95.4 | 91.3 | 92.0 | 91.5 | 97.3 | 91.5 | 91.5 | 97.0 | 81.0 | 98.0 | 100.0 |
| Sample Duplicate (Sample 19678) | %RPD | 23.6 | 24.0 | 189.8 | 142.3 | 15.6 | 7.0 | 50.0 | 15.2 | (1) | (1) | (1) |
| Spike Recovery | % Recovered | 104.0 | 77.5 | 113.5 | (2) | (2) | (2) | 62.5 | (2) | 106.0 | | |

| TCLP Leachates | UNITS | ICP ANALYSES | | | | | | | | AA ANALYSES | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Cd | Cr | Cu | Fe | Pb | Mn | Ni | Zn | As | Se | Hg |
| Reference Standard | % Recovered | 106.0 | 106.3 | 103.5 | 105.0 | 104.2 | 104.0 | 105.0 | 105.0 | 108.7 | 95.6 | 90.9 |
| Calibration Blank | ug/L | <10 | <5 | <5 | <5 | <50 | 1.2 | <15 | <3 | <10 | <5 | <2 |
| Reagent Blank 1 | ug/L | <10 | <5 | 7.6 | 2.5 | <50 | 3.9 | <15 | 48 | <10 | <5 | <2 |
| Check Standard | % Recovered | 95.1 | 89.7 | 92.0 | 92.0 | 100.2 | 92.5 | 90.5 | 97.0 | 118.0 | 92.0 | 104.0 |
| Sample Duplicate (Sample 19517) | %RPD | 196.5 | (1) | (1) | 138.1 | 154.2 | 95.5 | 84.0 | 153.3 | (1) | (1) | (1) |
| Spike Recovery | % Recovered | (2) | 102.0 | 113.2 | (2) | (2) | (2) | 51.0 | (2) | 108.0 | 82.0 | |

## TABLE 4.15 QC SUMMARY (INTERNAL) FOR METALS

| SW - 924 (Extraction 1) Leachates | UNITS | ICP ANALYSES | | | | | | | | AA ANALYSES | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Cd | Cr | Cu | Fe | Pb | Mn | Ni | Zn | As | Se | Hg |
| Reference Standard | % Recovered | 99.4 | 97.2 | 98.5 | 95.0 | 96.4 | 96.0 | 98.0 | 97.5 | 104.3 | 87.6 | 97.7 |
| Calibration Blank | ug/L | <10 | <5 | <5 | <5 | <50 | <1 | <15 | <3 | <10 | <5 | <2 |
| Reagent Blank 1 | ug/L | <10 | 8.8 | <5 | 34 | <50 | 1.6 | <15 | 22 | <10 | <5 | <20 |
| Reagent Blank 2 | ug/L | <10 | 5.3 | <5 | 25 | <50 | <1 | <15 | 5.2 | | | |
| Check Standard | % Recovered | 102.1 | 98.8 | 99.5 | 95.5 | 100.7 | 98.5 | 98.0 | 100.5 | 110.0 | 86.0 | 104.0 |
| Sample Duplicate (Sample 19517) | %RPD | (1) | (1) | 0.0 | (1) | 16.1 | 62.5 | (1) | 88.2 | (1) | 42.7 | (1) |
| Spike Recovery | % Recovered | 82.0 | 82.0 | 73.0 | 96.0 | 104.0 | | 82.0 | 72.0 | 124.0 | 60.0 | |

| SW - 924 (Extraction 2) Leachates | UNITS | ICP ANALYSES | | | | | | | | AA ANALYSES | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Cd | Cr | Cu | Fe | Pb | Mn | Ni | Zn | As | Se | Hg |
| Reference Standard | % Recovered | 102.1 | 98.8 | 99.5 | 95.5 | 100.7 | 98.5 | 98.0 | 100.5 | 108.7 | 87.6 | 88.6 |
| Calibration Blank | ug/L | <10 | <5 | <5 | <5 | <50 | <1 | <15 | <3 | <10 | <5 | <2 |
| Reagent Blank 1 | ug/L | <10 | 7.3 | 1.1 | 22 | <50 | 1.6 | <15 | 16 | <10 | <5 | <20 |
| Reagent Blank 2 | ug/L | <10 | 6.6 | 5 | 11 | <50 | 1.1 | <15 | <3 | | | |
| Check Standard | % Recovered | 103.3 | 97.6 | 98.5 | 96.0 | 96.0 | 96.5 | 96.5 | 98.5 | 107.0 | 100.0 | 104.0 |
| Sample Duplicate (Sample 19521) | %RPD | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) |
| Spike Recovery | % Recovered | 83.0 | 93.0 | 88.0 | 126.0 | 95.0 | 84.0 | 87.0 | 87.0 | 100.0 | 136.0 | |

NOTES:

(1) One or both values at or below the method detection limit.
(2) Spike less than 10% of the sample concentration.

the project were an RPD between duplicate analyses of 0-20 percent, and an accuracy (% recovery of spikes) of 75 to 125 percent in conformance to the EPA Contract Laboratory Program.

No significant problems were encountered in maintaining calibration or with contamination of reagents or laboratory water. Occasionally , some metals were detected in calibration and reagent blanks in the low microgram per liter (ug/L) range. Normally, no corrections of the sample analytical results for the blanks were required.

The precision criteria (RPD on duplicates) were generally achieved with some exceptions. In the analyses of field water samples, Fe exceeded the criteria in analysis of Batches 1-4, Zn exceeded the criteria in analysis of Batch 5, and Cu and Mn exceeded the criteria in analysis of Batch 6. In the analyses of laboratory-prepared leachates, the Versar laboratory encountered difficulty in achieving the criteria in analyses for Cd, Cr, Cu, Fe and Ni in the EP leachate, Cd, Fe, Pb, Mn, Ni and Zn in the TCLP leachate, and Mn, Zn, and Se in the first extract by the MWEP. The problems with the analysis of laboratory leachates may have been related to the relatively low concentration levels for some of these metals in the leachates and the inherent increased variability at these low levels.

The accuracy criteria (% recovery of spikes) were also generally achieved with few exceptions. In the analysis of the solid residue digestates, the criteria for Cr was below the lower limit. In the analyses of field water samples, the criteria for Pb was below the lower limit in Batch 5, and the criteria for Cu and Pb were below the lower limit in Batch 6. In the analyses of the laboratory-prepared leachates, the criteria for Ni was below the lower limit in the EP leachates and the TCLP leachates, the criteria for Cu, Zn and Se were below the criteria in the first extract by the MWEP, and the criteria for Hg was slightly above the upper limit in the second extract by the MWEP.

Overall, however, the analyses for total metals in all matrices were in control. The data from the analyses of samples are, therefore, considered valid. Corrective actions were taken by the laboratory on each occasion of a criteria exceedance in accordance with the Quality Assurance Project Plan. These corrective actions maintained control in the total metals analyses.

4.5.1.2 Polychlorinated Biphenyls - Analyses of solid residues and selected field water samples for polychlorinated biphenyls (PCBs) were conducted by the Versar laboratory. Samples were analyzed in three separate groups at different times. The first group of samples consisted of all fly ash samples collected at the four facilities. The second group of samples consisted of selected field water samples including quench water, leachates collected at the monofilled landfills, and ground water. The third group of samples consisted of other ash samples including bottom and combined bottom/fly ash, size fractions of fly ash samples collected at Facility C, and composite samples collected from the monofilled landfill at Facilities C and D. Analyses of each group (except as noted below) were accompanied by internal QC checks consisting of the following: (1) analysis of reagent blanks, (2) determination of the recoveries of four isotopically-labeled (carbon$^{13}$) isomers added as surrogate spikes to all samples prior to extraction to track the performance of the extraction, cleanup, and analysis of each sample, and (3) determination of the recoveries of matrix spike (MS) and matrix spike duplicates (MSD) on two field water samples. The MS and MSD consists of a mixture of Arochlors 1016 and 1260 and are used to determine accuracy and precision. No criteria for the recovery of surrogate spikes or for the relative percent difference (RPD) between the matrix spikes and matrix spike duplicates have been established for this method.

The results of these internal QC checks for the PCB analyses are summarized in Table 4.16 and are discussed below.

No PCBs were detected in any of the laboratory reagent blanks accompanying each group of samples analyzed, indicating that the laboratory water and reagents were free of PCB contamination.

## TABLE 4.16 QC SUMMARY (INTERNAL) FOR PCB ANALYSIS

|  |  |  |  | Surrogate Recovery (%) |  |  |  |
|---|---|---|---|---|---|---|---|
| Facility | Sample Matrix | Sample Description | Sample Number | 4-Chloro-Biphenyl | 3,3',4,4' Tetrachloro Biphenyl | Octa Chloro Biphenyl | Deca Chloro Biphenyl |
| A | Fly | Unit 1, 9/26, AM | 17628 | 3 | 0 | 87 | 95 |
| A | Fly | Unit 1, 9/26, AM, Dup | 17631 | 0 | 1.4 | 80 | 108 |
| A | Fly | Unit 1, 9/26, PM | 17637 | 0 | 4 | 74 | 83 |
| A | Fly | Unit 2, 9/26, AM | 17643 | 9 | 9 | 29 | 33 |
| A | Fly | Unit 2, 9/26, PM | 17646 | 1 | 0 | 68 | 80 |
| A | Bottom/Fly | Unit 1, 9/26, AM | 17625 | 51 | 69 | 73 | 72 |
| A | Bottom/Fly | Unit 1, 9/26, PM | 17640 | 64 | 105 | 107 | 78 |
| A | Bottom/Fly | Unit 1, 9/26, PM | 17640MS | 57 | 94 | 94 | 90 |
| A | Bottom/Fly | Unit 1, 9/26, PM | 17640MSD | 48 | 75 | 75 | 65 |
| A | Bottom/Fly | Unit 2, 9/26, AM | 17619 | 54 | 68 | 66 | 55 |
| A | Bottom/Fly | Unit 2, 9/26, AM, Dup | 17622 | 66 | 76 | 70 | 59 |
| A | Bottom/Fly | Unit 2, 9/26, PM | 17634 | 67 | 82 | 74 | 56 |
| A | Quench | Unit 1, 9/26 | 17546-47 | 74 | 90 | 78 | 79 |
| A | Quench | Unit 2, 9/26 | 17556-57 | 52 | 71 | 65 | 67 |
| B | Fly | Unit 3, 9/28, AM | 17669 | 0 | 0 | 78 | 77 |
| B | Fly | Unit 3, 9/28, AM, Dup | 17672 | 0 | 0 | 60 | 49 |
| B | Fly | Unit 3, 9/29, PM | 17693 | 3 | 1 | 82 | 82 |
| B | Fly | Unit 4, 9/28, AM | 17680 | 0 | 0.3 | 68 | 72 |
| B | Fly | Unit 4, 9/29, PM | 17686 | 0 | 0 | 15 | 17 |
| B | Fly | Unit 4, 9/29, PM | 17686MSD | 3 | 3 | 85 | 86 |
| B | Fly | Unit 4, 9/29, PM | 17686MS | 0.3 | 0 | 68 | 74 |
| B | Bottom | Unit 3, 9/28, AM | 17666 | 59 | 84 | 93 | 72 |
| B | Bottom | Unit 3, 9/29, PM | 17690 | 65 | 76 | 106 | 104 |
| B | Bottom | Unit 4, 9/28, AM | 17674 | 34 | 48 | 69 | 67 |
| B | Bottom | Unit 4, 9/28, AM, Dup | 17677 | 60 | 75 | 92 | 87 |
| B | Bottom | Unit 4, 9/29, PM | 17683 | 71 | 78 | 101 | 82 |
| B | Quench | Unit 3, 9/28 | 17596-97 | 56 | 71 | 60 | 66 |
| B | Quench | Unit 4, 9/28 | 17606-07 | 74 | 94 | 113 | 129 |
| B | Quench | Unit 4, 9/28, Dup | 17536-37 | 98 | 111 | 139 | 165 |
| B | Leachate | East Side | 19837-38 | 59 | 84 | 78 | 83 |
| B | Leachate | North Side | 19859-60 | 66 | 98 | 87 | 83 |
| B | Leachate | Northeast Corner | 19846-47MSD | 54 | 71 | 60 | 60 |
| B | Leachate | Northeast Corner | 19846-47MS | 56 | 87 | 69 | 42 |
| B | Leachate | Northeast Corner | 19846-47 | 55 | 83 | 58 | 62 |

## TABLE 4.16 QC SUMMARY (INTERNAL) FOR PCB ANALYSIS

### Surrogate Recovery (continued)

| Facility | Sample Matrix | Sample Description | Sample Number | 4-Chloro-Biphenyl | 3,3',4,4' Tetrachloro Biphenyl | Octa Chloro Biphenyl | Deca Chloro Biphenyl |
|---|---|---|---|---|---|---|---|
| C | Fly | Unit 2, 9/28, PM | 19519 | 32 | 42 | 82 | 63 |
| C | Fly | Unit 2, 9/29, PM | 19543 | 98 | 76 | 128 | 109 |
| C | Fly | Unit 2, 9/29, PM, Dup | 19546 | 40 | 51 | 96 | 84 |
| C | Fly | Unit 2, 9/30, AM | 19585 | 52 | 64 | 77 | 87 |
| C | Fly | Unit 2, 9/30, PM | 19598 | 112 | 121 | 129 | 85 |
| C | Fly | Unit 2, Coarse | 19549 | 0.2 | 0 | 82 | 74 |
| C | Fly | Unit 2, Fine (ESP) | 19555 | 11 | 9 | 76 | 80 |
| C | Fly | Unit 2, Medium | 19552 | 41 | 70 | 96 | 87 |
| C | Bottom/Fly | Unit 2, 9/28, PM | 19515 | 86 | 81 | 100 | 87 |
| C | Bottom/Fly | Unit 2, 9/29, PM | 19540 | 51 | 75 | 83 | 88 |
| C | Bottom/Fly | Unit 2, 9/30, AM | 19588 | 70 | 84 | 79 | 85 |
| C | Bottom/Fly | Unit 2, 9/30, AM, Dup | 19590 | 60 | 87 | 87 | 79 |
| C | Bottom/Fly | Unit 2, 9/30, PM | 19595 | 10 | 21 | 23 | 21 |
| C | Landfill | Perimeter Composite | 19523 | 267 | 159 | 111 | 45 |
| C | Leachate | North Side | 19805-06 | 68 | 91 | 82 | 88 |
| C | Leachate | Northeast Corner | 19793-94 | 59 | 109 | 107 | 87 |
| C | Leachate | Northeast Corner | 19817-18 | 32 | 33 | 30 | 26 |
| C | MWell | #17 | 19785-86MSD | 106 | 113 | 105 | 81 |
| C | MWell | #17 | 19785-86 | 63 | 103 | 114 | 109 |
| C | MWell | #17 | 19785-86MS | 98 | 116 | 103 | 85 |
| C | MWell | #3 | 19759-60 | 64 | 115 | 97 | 77 |
| C | MWell | #4 | 19772-73 | 58 | 102 | 96 | 78 |
| C | PWell | Production Well | 19579-80 | 72 | 113 | 132 | 120 |
| C | Quench | Unit 2, 9/28 | 19509-10 | 130 | 180 | 170 | 107 |
| C | Quench | Unit 2, 9/30 | 19566-67 | 62 | 85 | 86 | 105 |
| D | Fly | Unit 1-2, 10/3, AM | 19669 | 44 | 36 | 80 | 92 |
| D | Fly | Unit 1-2, 10/3, AM, Dup | 19672 | 43 | 27 | 136 | 156 |
| D | Fly | Unit 1-2, 10/3, PM | 19681 | 14 | 7 | 97 | 124 |
| D | Fly | Unit 1-2, 10/4, AM | 19687 | 53 | 50 | 104 | 97 |
| D | Fly | Unit 1-2, 10/4, PM | 19708 | 23 | 20 | 73 | 75 |
| D | Bottom/Fly | Unit 1-2, 10/3, AM | 19677 | 40 | 94 | 102 | 76 |
| D | Bottom/Fly | Unit 1-2, 10/3, PM | 19684MSD | 64 | 104 | 105 | 86 |
| D | Bottom/Fly | Unit 1-2, 10/3, PM | 19684MS | 66 | 94 | 102 | 86 |
| D | Bottom/Fly | Unit 1-2, 10/3, PM | 19684 | 61 | 90 | 89 | 98 |
| D | Bottom/Fly | Unit 1-2, 10/4, AM | 19690 | 1 | 99 | 86 | 66 |
| D | Bottom/Fly | Unit 1-2, 10/4, AM, Dup | 19693 | 54 | 113 | 99 | 66 |
| D | Bottom/Fly | Unit 1-2, 10/4, PM | 19712 | 59 | 87 | 78 | 58 |
| D | Landfill | Perimeter Composite | 19600 | 59 | 86 | 80 | 61 |
| D | Leachate | Northeast Corner | 19623-24 | 52 | 101 | 114 | 93 |
| D | Leachate | Northeast Corner | 19636-37 | 48 | 90 | 95 | 51 |
| D | Leachate | Southeast Corner | 19610-11 | 64 | 75 | 80 | 86 |
| D | Quench | Unit 2, 10/3 | 19649-50 | 50 | 81 | 65 | 62 |
| D | Quench | Unit 2, 10/3, Dup | 19662-63 | 50 | 102 | 92 | 105 |
| D | Quench | Unit 2, 10/4 | 19703,27 | 42 | 57 | 60 | 39 |

## TABLE 4.16 QC SUMMARY (INTERNAL) FOR PCB ANALYSIS

### Surrogate Recovery (continued)

| Facility | Sample Matrix | Sample Description | Sample Number | 4-Chloro-Biphenyl | 3,3',4,4' Tetrachloro Biphenyl | Octa Chloro Biphenyl | Deca Chloro Biphenyl |
|---|---|---|---|---|---|---|---|
|  | Blank | Laboratory | RB#310 | 50 | 61 | 56 | 36 |
|  | Blank | Laboratory | RB#576 | 42 | 76 | 90 | 84 |
|  | Blank | Laboratory | RB#578 | 31 | 86 | 97 | 96 |
|  | Blank | Laboratory | RB#917 | 21 | 93 | 96 | 103 |
|  | Blank | Laboratory | RB#633 | 59 | 88 | 99 | 83 |
|  | Blank | Laboratory | RB#635 | 54 | 92 | 93 | 86 |

### Matrix Spike Results for PCB Analyses

|  |  |  |  | MS | MSD | RPD |
|---|---|---|---|---|---|---|
| B | Leachate | Northeast Corner | 19846-47 | 45 | 42 | 2 |
| C | MWell | #17 | 19785-86 | 75 | 78 | 3 |
| A | Bottom/Fly | Unit 1, 9/26, PM | 17640 |  |  |  |
| D | Bottom/Fly | Unit 1-2, 10/3, PM | 19684 |  |  |  |

The Versar laboratory experienced significant difficulties with the analyses of the first group of samples consisting of 20 fly ash samples. The problems are summarized in Section 3.4.2 of this report and detailed in the data appendices. The problems are reflected in poor recoveries of the lower molecular weight surrogate spikes (4-chlorobiphenyl and 3,3',4,4' tetrachlorobiphenyl) from the fly ash samples collected at Facilities A and B. After some adjustments to the procedures for cleanup of the extracts, recoveries of these surrogate spikes were improved as is reflected in the recoveries from the fly ash samples collected at Facilities C and D. However, the problems with poor recoveries of the lower molecular weight surrogate spikes recurred in some of the bottom and combined bottom/fly ash samples analyzed in Group 3. The recoveries of the higher molecular weight (octachloro and decachloro biphenyls) surrogate spikes were consistently better than those for the lower molecular weight surrogate spikes in the fly ash samples. Recoveries ranged from 15 percent to 135 percent for octachloro biphenyl and 17 percent to 156 percent for decachloro biphenyl.

Recoveries of all surrogate spikes from the field water samples (analyzed as Group 2) were good; ranges are as follows: 4-chlorobiphenyl, 32 percent to 130 percent; tetrachloro biphenyl, 33 percent to 180 percent; octachloro biphenyl, 30 percent to 139 percent; decachloro biphenyl, 26 percent to 120 percent.

The Versar laboratory again experienced some problems with recoveries of the lower molecular weight surrogate spikes in the analyses of the other ash samples (Group 3). The recoveries of 4-chloro biphenyl were 10 percent or less for three samples, and the recoveries of tetrachloro biphenyl were 10 percent or less for two samples. The poor recoveries were largely associated with analyses of the coarse and fine fly ash samples from Facility C. With these exceptions, however, recoveries were good, with ranges as follows: 4-chloro biphenyl, 11 percent to 267 percent; tetrachloro biphenyl, 21 percent to 159 percent; octachloro biphenyl, 23 percent to 111 percent; decachloro biphenyl, 21 percent to

104 percent. The poor recoveries for some QC samples may be related to the strong attractive force which causes the PCBs to be absorbed onto the surface of the solid substrates (i.e., fly ash particles).

The recoveries of matrix spikes and matrix spike duplicates using a 50/50 mixture of native Arochlor 1016 and 1260 as the spikes were determined on two field water samples. Due to the problems encountered initially in the analyses of the fly ash samples (Group 1) matrix spikes, no duplicates were analyzed for the ash samples.

The recoveries on the matrix spikes (MS) and matrix spike duplicates (MSD), and the relative percent difference (RPD) between the two spikes were excellent for the liquid samples indicating good precision in the analyses. The recoveries of the matrix spikes of the ash samples were 51 percent, 100 percent, and 92 percent.

The analyses of PCB homologs in fly ash samples (Group 1), field water samples (Group 2), and other ash samples (Group 3) overall were in control, with one exception. The analyses for the lower molecular weight PCB homologs (tetrachloro biphenyls) in the fly ash samples from Facilities A and B (analyzed in Group 1) were not in control. The results of analyses for the lower molecular weight PCB homologs in these samples are probably biased toward low values due to poor surrogate spike recoveries. The results of analyses for the higher molecular weight PCB homologs (pentachloro biphenyls and more chlorinated) in all samples are probably as accurate as current methodology is capable of achieving. The results of analyses for the lower molecular weight PCB homologs (tetrachloro biphenyl and lighter) in all samples except the fly ash samples from Facilities A and B are accurate for the intended use of the data.

4.5.1.3 PCDD/PCDFs - Analyses for solid residues, selected field water samples, and TCLP leachates of selected solid residue samples for PCDDs and PCDFs were performed by Versar's subcontract laboratory, Battelle, Columbus. Analyses of each batch of samples for each matrix were accompanied by internal QC checks consisting of the following: analysis of method blanks, determination of recoveries of five isotopically-labeled PCDD and four isotopically-labeled PCDF internal standards added to each sample, blank and native spike sample prior to extraction and analyses, and determination of recoveries of native PCDD/PCDF spikes in 1 sample per batch (frequency of 5 percent). The results of the recovery of the nine isotopically labeled internal standards are presented in Table 4.17.

Native spike and laboratory method blank samples were processed during the extraction and cleanup of the samples. The native spike sample was used to evaluate accuracy, while the laboratory method blank samples were used to demonstrate the absence of contamination.

The samples were analyzed in three batches. The first batch consisted of 20 fly ash samples from the four facilities. The second batch consisted of bottom ash or combined bottom/fly ash from the four facilities, composites of sample collected from the perimeter of landfills at Facilities C and D, and coarse and fine fractions of a fly ash sample from Facility C. The third batch consisted of field waters (field leachate and quench water samples) and leachates prepared in the laboratory by the TCLP method using selected samples of fly ash and bottom ash, or combined bottom/fly ash from the four facilities.

In the first batch of 20 fly ash samples, the method blank analyses were free of PCDD/PCDF contamination, except for trace levels of hepta-CDD and octa-CDD. The observed levels were less than the desired detection limit for these congener classes and should, therefore, not adversely affect the analytical results. Recovery of the analytes from the native spike samples ranged from 90 to 110 percent, which is within the expected range of variation, and within the QC criteria specified in the Quality Assurance Project Plan (QAPP).

The recoveries of the nine isotopically-labeled internal standards in fly ash samples were used to correct analytical results for extraction

## TABLE 4.17 QC SUMMARY (INTERNAL) FOR PCDD/PCDF ANALYSIS

| | | | | Internal Standard (%) Recovery | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Facility | Sample Matrix | Sample Description | PCDD/ PCDF No. | TETRA -CDD | PENTA -CDD | HEXA -CDD | HEPTA -CDD | OCTA -CDD | TETRA -CDF | PENTA -CDF | HEXA -CDF | HEPTA -CDF |
| A | Fly Ash | Unit 1, 9/26, AM | 17629 | 89 | 81 | 57 | 74 | 76 | 85 | 89 | 15 | 13 |
| A | Fly Ash | Unit 1, 9/26, AM, Dup | 17632 | 92 | 80 | 58 | 76 | 72 | 94 | 90 | 24 | 20 |
| A | Fly Ash | Unit 1, 9/26, PM | 17638 | 74 | 79 | 59 | 67 | 63 | 86 | 86 | 22 | 17 |
| A | Fly Ash | Unit 2, 9/26, AM | 17644 | 120 | 125 | 85 | 94 | 93 | 154 | 128 | 5 | 5 |
| A | Fly Ash | Unit 2, 9/26, PM | 17647 | 84 | 61 | 46 | 44 | 37 | 85 | 70 | 45 | 42 |
| A | Bottom/Fly | Unit 2, 9/26, AM | 17620 | 82 | 99 | 95 | 98 | 100 | 82 | 90 | 83 | 86 |
| A | Bottom/Fly | Unit 1, 9/26, AM | 17624 | 84 | 76 | 71 | 64 | 61 | 85 | 79 | 66 | 62 |
| A | Bottom/Fly | Unit 2, 9/26, PM | 17635 | 89 | 100 | 99 | 98 | 99 | 99 | 98 | 85 | 85 |
| A | Bottom/Fly | Unit 2, 9/26, AM | 17620 | 32 | 27 | 34 | 36 | 40 | 32 | 31 | 31 | 36 |
| A | Bottom/Fly | Unit 2, 9/26, AM | 17620, | 110 | 110 | 93 | 110 | 120 | 110 | 100 | 100 | 110 |
| A | Fly Ash | Lab Leachate (TCLP) | 17644 | 94 | 110 | 89 | 86 | 87 | 94 | 100 | 92 | 92 |
| A | Quench | Unit 2, 9/26 | 17552-5 | 97 | 100 | 110 | 120 | 130 | 100 | 110 | 96 | 110 |
| A | Quench | Unit 1, 9/26 | 17542-4 | 98 | 97 | 100 | 100 | 110 | 99 | 100 | 100 | 110 |
| B | Fly | Unit 3, 9/28, AM | 17668 | 83 | 55 | 50 | 50 | 41 | 95 | 73 | 48 | 46 |
| B | Fly | Unit 3, 9/28, AM, Dup | 17671 | 89 | 74 | 62 | 66 | 56 | 100 | 87 | 64 | 63 |
| B | Fly | Unit 4, 9/28, AM | 17681 | 71 | 75 | 58 | 69 | 77 | 88 | 72 | 62 | 48 |
| B | Fly | Unit 4, 9/29, PM | 17687 | 85 | 75 | 56 | 43 | 20 | 88 | 78 | 54 | 44 |
| B | Fly | Unit 3, 9/29, PM | 17692 | 98 | 115 | 53 | 80 | 43 | 109 | 109 | 11 | 52 |
| B | Bottom | Unit 4, 9/28, AM | 17675 | 72 | 82 | 74 | 72 | 65 | 69 | 75 | 67 | 69 |
| B | Bottom | Unit 4, 9/28, AM, Dup | 17678 | 92 | 82 | 74 | 67 | 61 | 87 | 79 | 65 | 61 |
| B | Bottom | Unit 3, 9/28, AM | 17665 | 89 | 83 | 78 | 75 | 71 | 88 | 79 | 69 | 68 |
| B | Bottom | Unit 4, 9/29, PM | 17684 | 52 | 96 | 94 | 91 | 96 | 44 | 77 | 87 | 87 |
| B | Bottom | Unit 3, 9/29, PM | 17689 | 92 | 88 | 86 | 84 | 80 | 91 | 86 | 74 | 73 |
| B | Bottom Ash | Lab Leachate (TCLP) | 17675 | 99 | 94 | 85 | 95 | 104 | 90 | 90 | 91 | 94 |
| B | Fly Ash | Lab Leachate (TCLP) | 17681 | 93 | 98 | 100 | 110 | 120 | 96 | 104 | 99 | 110 |
| B | Leachate | North Side | 19865-6 | 33 | 37 | 30 | 30 | 30 | 31 | 33 | 31 | 32 |
| B | Leachate | Northeast Corner | 19852-5 | 89 | 87 | 72 | 70 | 71 | 90 | 90 | 74 | 70 |
| B | Leachate | East Side | 19839-4 | 92 | 102 | 95 | 100 | 109 | 94 | 92 | 97 | 104 |
| B | Quench | Unit 4, 9/28, Dup | 17532-3 | 70 | 71 | 60 | 57 | 58 | 70 | 64 | 60 | 59 |
| B | Quench | Unit 4, 9/28 | 17602-0 | 92 | 110 | 110 | 120 | 130 | 89 | 100 | 110 | 120 |

## TABLE 4.17 QC SUMMARY (INTERNAL) FOR PCDD/PCDF ANALYSIS

Internal Standard Recovery (continued)

| Facility | Sample Matrix | Sample Description | PCDD/ PCDF No. | TETRA -CDD | PENTA -CDD | HEXA -CDD | HEPTA -CDD | OCTA -CDD | TETRA -CDF | PENTA -CDF | HEXA -CDF | HEPTA -CDF |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C | Fly | Unit 2, 9/28, PM | 19520 | 90 | 89 | 35 | 95 | 65 | 108 | 84 | 20 | 62 |
| C | Fly | Unit 2, 9/29, PM | 19544 | 100 | 79 | 25 | 132 | 126 | 101 | 71 | 14 | 86 |
| C | Fly | Unit 2, 9/29, PM, Dup | 19547 | 96 | 94 | 50 | 102 | 57 | 97 | 95 | 5 | 67 |
| C | Fly | Unit 2, 9/30, AM | 19584 | 85 | 132 | 107 | 106 | 51 | 102 | 125 | 30 | 16 |
| C | Fly | Unit 2, 9/30, PM | 19597 | 113 | 78 | 30 | 113 | 24 | 119 | 78 | 7 | 5 |
| C | Bottom/Fly | Unit 2, 9/30, PM | 19594 | 63 | 73 | 75 | 60 | 56 | 68 | 75 | 71 | 59 |
| C | Bottom/Fly | Unit 2, 9/30, AM, Dup | 19590 | 78 | 92 | 80 | 87 | 84 | 78 | 83 | 74 | 77 |
| C | Bottom/Fly | Unit 2, 9/28, PM | 19516 | 78 | 80 | 72 | 66 | 58 | 71 | 77 | 64 | 65 |
| C | Bottom/Fly | Unit 2, 9/29, PM | 19541 | 74 | 75 | 73 | 66 | 67 | 75 | 73 | 45 | 60 |
| C | Bottom/Fly | Unit 2, 9/30, AM | 19587 | 85 | 72 | 66 | 67 | 62 | 72 | 65 | 56 | 59 |
| C | Fly | Unit 2, coarse | 19550 | 47 | 57 | 45 | 29 | 15 | 38 | 45 | 48 | 33 |
| C | Fly | Unit 2, fine (ESP) | 19556 | 62 | 30 | 18 | 26 | 20 | 56 | 30 | 18 | 20 |
| C | Landfill | Perimeter Composite (M) | 19524 | 110 | 94 | 83 | 68 | 58 | 100 | 95 | 73 | 63 |
| C | Landfill | Perimeter Composite (M) | 19524 | 90 | 62 | 77 | 67 | 65 | 85 | 60 | 63 | 64 |
| C | Bottom/Fly | Lab Leachate (TCLP) | 19541 | 98 | 86 | 76 | 75 | 82 | 91 | 89 | 73 | 74 |
| C | Fly Ash | Lab Leachate (TCLP) | 19550 | 100 | 110 | 97 | 97 | 98 | 100 | 100 | 93 | 100 |
| C | Leachate | North Side | 19807-1 | 97 | 110 | 79 | 76 | 82 | 89 | 89 | 81 | 76 |
| C | Leachate | Northeast Corner | 19799-0 | 91 | 81 | 55 | 47 | 43 | 93 | 78 | 56 | 49 |
| C | Leachate | Northwest Corner | 19819-2 | 83 | 120 | 100 | 100 | 120 | 83 | 93 | 100 | 110 |
| C | Quench | Unit 2, 9/30 | 19562-6 | 100 | 130 | 100 | 100 | 120 | 94 | 110 | 96 | 100 |
| C | Quench | Unit 2, 9/28 | 19505-0 | 91 | 110 | 78 | 80 | 76 | 89 | 95 | 83 | 81 |
| D | Fly | Unit 1-2, 10/3, AM | 19668 | 95 | 60 | 30 | 87 | 106 | 95 | 59 | 7 | 6 |
| D | Fly | Unit 1-2, 10/3, AM, Dup | 19671 | 90 | 74 | 29 | 83 | 91 | 95 | 71 | 17 | 54 |
| D | Fly | Unit 1-2, 10/3, PM | 19680 | 75 | 95 | 77 | 91 | 101 | 90 | 99 | 24 | 22 |
| D | Fly | Unit 1-2, 10/4, AM | 19686 | 93 | 109 | 54 | 106 | 109 | 98 | 106 | 11 | 9 |
| D | Fly | Unit 1-2, 10/4, PM | 19707 | 97 | 101 | 87 | 101 | 129 | 94 | 98 | 31 | 31 |
| D | Bottom/Fly | Unit 1-2, 10/4, AM | 19689 | 91 | 92 | 77 | 77 | 80 | 88 | 91 | 78 | 79 |
| D | Bottom/Fly | Unit 1-2, 10/4, PM | 19711 | 88 | 81 | 76 | 78 | 80 | 89 | 80 | 65 | 68 |
| D | Bottom/Fly | Unit 1-2, 10/3, AM | 19676 | 86 | 83 | 77 | 80 | 78 | 85 | 78 | 70 | 73 |
| D | Bottom/Fly | Unit 1-2, 10/3, PM | 19683 | 68 | 75 | 70 | 69 | 61 | 68 | 71 | 65 | 64 |
| D | Landfill | Perimeter Composite (H) | 19601 | 83 | 78 | 73 | 69 | 68 | 81 | 75 | 62 | 61 |
| D | Bottom/Fly | Lab Leachate (TCLP) | 19676 | 100 | 120 | 96 | 92 | 96 | 100 | 110 | 100 | 100 |
| D | Fly Ash | Lab Leachate (TCLP) | 19668 | 110 | 97 | 100 | 98 | 100 | 99 | 110 | 98 | 100 |
| D | Leachate | Northeast Corner | 19632-3 | 94 | 99 | 70 | 63 | 59 | 99 | 92 | 65 | 63 |
| D | Leachate | Northeast Corner | 19619-2 | 96 | 89 | 69 | 59 | 56 | 100 | 89 | 68 | 59 |
| D | Quench | Unit 2, 10/3, Dup | 19657-6 | 95 | 94 | 78 | 80 | 84 | 95 | 89 | 78 | 79 |
| D | Quench | Unit 2, 10/4 | 19698-0 | 111 | 114 | 82 | 72 | 64 | 88 | 99 | 76 | 69 |
| D | Quench | Unit 2, 10/3 | 19644-4 | 64 | 63 | 48 | 44 | 43 | 68 | 64 | 49 | 44 |

## TABLE 4.17 QC SUMMARY (INTERNAL) FOR PCDD/PCDF ANALYSIS

Internal Standard Recovery (continued)

| Facility | Sample Matrix | Sample Description | PCDD/ PCDF No. | TETRA -CDD | PENTA -CDD | HEXA -CDD | HEPTA -CDD | OCTA -CDD | TETRA -CDF | PENTA -CDF | HEXA -CDF | HEPTA -CDF |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | blank | Laboratory #1 | | 84 | 65 | 52 | 54 | 57 | 77 | 68 | 47 | 49 |
| | blank | Laboratory #2 | | 97 | 32 | 85 | 96 | 114 | 102 | 96 | 43 | 44 |
| | spike | Native Laboratory #1 | | 95 | 72 | 49 | 58 | 62 | 83 | 72 | 13 | 12 |
| | spike | Native Laboratory #2 | | 95 | 109 | 93 | 102 | 120 | 88 | 108 | 80 | 81 |
| | blank | Method Blank #1 | | 84 | 97 | 90 | 88 | 83 | 81 | 86 | 86 | 83 |
| | blank | Method Blank #2 | | 90 | 100 | 78 | 79 | 81 | 91 | 82 | 76 | 83 |
| | blank | Method Blank #3 | | 82 | 110 | 95 | 89 | 100 | 95 | 99 | 95 | 94 |
| | blank | Method Blank #4 | | 88 | 83 | 85 | 90 | 88 | 90 | 85 | 79 | 82 |
| | blank | Method Blank #5 | | 76 | 81 | 75 | 70 | 74 | 73 | 69 | 67 | 70 |
| | blank | Method Blank #6 | | 77 | 86 | 88 | 81 | 77 | 77 | 82 | 82 | 77 |
| | blank | Method Blank #7 | | 70 | 57 | 74 | 76 | 75 | 67 | 71 | 64 | 67 |
| | spike | Native Spike #1 | | 66 | 70 | 67 | 68 | 69 | 65 | 65 | 61 | 63 |
| | spike | Native Spike #2 | | 92 | 95 | 88 | 98 | 97 | 92 | 89 | 80 | 89 |
| | spike | Native Spike #3 | | 56 | 65 | 56 | 60 | 63 | 55 | 53 | 52 | 56 |
| | spike | Native Spike #4 | | 74 | 91 | 91 | 87 | 88 | 51 | 79 | 83 | 85 |
| | blank | Method Blank #1a | | 92 | 110 | 92 | 92 | 94 | 96 | 100 | 92 | 97 |
| | blank | Method Blank #2a | | 90 | 100 | 91 | 92 | 100 | 89 | 100 | 92 | 98 |
| | blank | Method Blank #3a | | 93 | 100 | 99 | 99 | 94 | 91 | 95 | 99 | 100 |
| | blank | Method Blank #4a | | 100 | 110 | 89 | 87 | 91 | 99 | 100 | 86 | 90 |
| | blank | Method Blank #5a | | 110 | 69 | 100 | 110 | 130 | 100 | 97 | 100 | 110 |
| | spike | Native Spike #1a | | 88 | 100 | 85 | 82 | 86 | 89 | 91 | 86 | 88 |
| | spike | Native Spike #2a | | 100 | 110 | 100 | 110 | 120 | 97 | 110 | 100 | 110 |
| | spike | Native Spike #3a | | 100 | 91 | 91 | 97 | 110 | 96 | 100 | 88 | 92 |
| | blank | TCLP Blank | | 75 | 80 | 63 | 62 | 67 | 66 | 69 | 61 | 64 |

efficiency and cleanup losses. The expected range of recoveries and QC criteria for recovery of the internal standards is 60 to 90 percent. The actual ranges of recoveries for the 20 fly ash samples plus two method blanks and two native spike samples is summarized below.

| INTERNAL STANDARD | RECOVERY RANGE % | NUMBER OF OUTSIDE QC CRITERIA Above | Below | Total |
|---|---|---|---|---|
| Tetra-CDD-$^{13}C_{12}$ | 71 - 120 | 12 | 0 | 12 |
| Penta-CDD-$^{13}C_{12}$ | 32 - 132 | 8 | 2 | 10 |
| Hexa-CDD-$^{13}C_{12}$ | 25 - 107 | 2 | 17 | 19 |
| Hepta-CDD-$^{13}C_{12}$ | 43 - 132 | 11 | 5 | 16 |
| Octa-CDD-$^{13}C_{12}$ | 20 - 129 | 9 | 9 | 17 |
| Tetra-CDF-$^{13}C_{12}$ | 77 - 154 | 15 | 0 | 15 |
| Penta-CDF-$^{13}C_{12}$ | 59 - 128 | 9 | 1 | 10 |
| Hexa-CDF-$^{13}C_{12}$ | 5 - 80 | 0 | 21 | 21 |
| Hepta-CDF-$^{13}C_{12}$ | 5 - 86 | 0 | 19 | 19 |

The narrow range of expected recoveries of the internal standards (60 to 90 percent) is typical of samples with relatively clean matrices and was not often achievable in the analyses of the fly ash samples. Because the internal standards are used to correct analytical results for extraction efficiency and cleanup losses, however, the failure to meet the QC criteria does not affect the quality of the data provided.

In the second batch of samples consisting of bottom ash, combined bottom/fly ash, and landfill composite samples, the method blank analyses were free of PCDD/PCDF contamination except for trace levels of octa-CDD. The observed levels were less than the desired detection limits for these congener classes and should, therefore, not adversely affect the analytical results. Recovery of the analytes from the native spike samples ranged from 90 to 110 percent, which is within the expected range of variation, and within the QC criteria specified in the QAPP for this project.

As with all analyses, the recoveries of the nine isotopically labeled internal standards in these samples were used to correct analytical results for extraction efficiency and cleanup losses. The expected range of recoveries and QC criteria for recoveries is 60 to 90 percent. The actual ranges of recoveries for the 22 samples in this batch, plus seven method blanks and four native spike samples is summarized below.

| INTERNAL STANDARD | RECOVERY RANGE % | NUMBER OF OUTSIDE QC CRITERIA Above | Below | Total |
|---|---|---|---|---|
| Tetra-CDD-$^{13}C_{12}$ | 47 - 110 | 5 | 3 | 8 |
| Penta-CDD-$^{13}C_{12}$ | 30 - 110 | 11 | 3 | 14 |
| Hexa-CDD-$^{13}C_{12}$ | 18 - 99 | 5 | 3 | 8 |
| Hepta-CDD-$^{13}C_{12}$ | 26 - 98 | 4 | 2 | 6 |
| Octa-CDD-$^{13}C_{12}$ | 15 - 100 | 5 | 5 | 10 |
| Tetra-CDF-$^{13}C_{12}$ | 38 - 100 | 6 | 5 | 11 |
| Penta-CDF-$^{13}C_{12}$ | 30 - 99 | 4 | 3 | 7 |
| Hexa-CDF-$^{13}C_{12}$ | 18 - 95 | 1 | 5 | 6 |
| Hepta-CDF-$^{13}C_{12}$ | 20 - 94 | 1 | 5 | 6 |

The recoveries of internal standards from the coarse and fine fractions of fly ash from Facility C were consistently below the QC criteria, as were the recoveries from native spike 3. The recoveries of internal standards from the remaining samples were generally within or above the QC criteria. Because the internal standards are used to correct analytical results for extraction efficiency and cleanup losses, however, the failure to meet the QC criteria does not affect the quality of the data provided.

In the third batch of samples consisting of field waters and laboratory prepared leachates, the method blank analyses were free of PCDD/PCDF contamination except for trace levels of octa-CDD. The observed levels were less than the desired detection limits for these congener classes and should, therefore, not adversely affect the analytical results. Recovery of the analytes from the native spike samples ranged from 90 to 100 percent, which is within the expected range of variation, and within the QC criteria specified in the QAPP for this project.

As with all analyses, the recoveries of the nine isotopically labeled internal standards in these samples were used to correct analytical results for extraction efficiency and cleanup losses. The expected range of recoveries is 60 to 90 percent. The actual range of recoveries for the 26 field waters and laboratory prepared leachates plus five method blanks, three native spike samples, and one TCLP blank is summarized below.

| INTERNAL STANDARD | RECOVERY RANGE % | NUMBER OF OUTSIDE QC CRITERIA Above | Below | Total |
|---|---|---|---|---|
| Tetra-CDD-$^{13}C_{12}$ | 32 - 111 | 26 | 2 | 28 |
| Penta-CDD-$^{13}C_{12}$ | 27 - 130 | 25 | 2 | 27 |
| Hexa-CDD-$^{13}C_{12}$ | 30 - 110 | 17 | 4 | 21 |
| Hepta-CDD-$^{13}C_{12}$ | 30 - 120 | 18 | 5 | 23 |
| Octa-CDD-$^{13}C_{12}$ | 30 - 130 | 19 | 7 | 26 |
| Tetra-CDF-$^{13}C_{12}$ | 31 - 110 | 21 | 2 | 23 |
| Penta-CDF-$^{13}C_{12}$ | 31 - 110 | 23 | 2 | 25 |
| Hexa-CDF-$^{13}C_{12}$ | 31 - 110 | 18 | 4 | 22 |
| Hepta-CDF-$^{13}C_{12}$ | 32 - 120 | 19 | 6 | 25 |

The recoveries of internal standards from most samples were above the QC criteria range indicating better than expected recoveries. The recoveries from the leachate prepared from Sample 17620 (bottom/fly ash from Facility A) and from the field leachate sample (19865-68) from Facility B, however, were consistently below the QC criteria. Because the internal standards are used to correct analytical results for extraction efficiency and cleanup losses, however, the failure to meet the QC criteria does not affect the quality of the data provided.

Overall, the analyses of samples for PCDDs and PCDFs were in control with very low levels of contamination in blanks, acceptable recoveries of analytes from native spike samples and generally acceptable to better than expected recoveries of isotopically labeled internal standards. These results are consistent with good quality analytical practice. The data is considered to be acceptable.

4.5.1.4 Organic Constituents - Analyses of selected field water samples and laboratory-prepared leachates for semi-volatile organic compounds (Base Neutral/Acid Extractable or BNAs) were performed by the Versar laboratory. Analyses of each batch of samples of each matrix were accompanied by internal QC checks consisting of the following analyses: analysis of laboratory blanks, determination of recoveries of six surrogate compounds which are readily identified in the GC/MS analysis and added to each sample before extraction to track the performance of the extraction and analysis, and determination of the recoveries of matrix spikes and matrix spike duplicates (the spikes are added to one sample per batch prior to extraction and analysis) to monitor the accuracy and precision of the analysis. The criteria for recovery of surrogates and the matrix spike and matrix spike duplicates are specified in the EPA Contract Laboratory Program and are listed in the summary tables in this section of this report.

The results of these internal QC checks for the BNA analyses of samples in this project are summarized in Table 4.18 and discussed below.

No semi-volatile organic compounds were detected in the BNA analyses of laboratory blanks for the field water samples indicating that the laboratory water and reagents were free of contamination by this group of compounds. Diethyl phthalate was detected in the blanks of the EP, TCLP and MWEP leachates prepared in the laboratory at concentrations from 8 to 24 ug/L. This is a common occurrence resulting from leaching of phthalates from plastic bottles used in preparation of the leachates. The blanks did not interfere with subsequent analyses.

## TABLE 4.18 QC SUMMARY (INTERNAL) FOR ORGANIC ANALYSIS

| | | | | Surrogate Recoveries (%) for Field Water Samples | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Facility | Sample Matrix | Sample Description | Sample Number | Nitro Benzene-D5 | 2-Fluoro-Biphenyl | Terphenyl -D4 | Phenol -D5 | 2-Fluoro-Phenol | 2,4,6-Tribromo Phenol |
| A | Quench | Unit 1, 9/26 | 17538 | 99 | 87 | 109 | 84 | 94 | 114 |
| A | Quench | Unit 2, 9/26 | 17548 | 87 | 74 | 85 | 86 | 86 | 86 |
| B | Quench | Unit 3, 9/28 | 17588 | 103 | 96 | 108 | 96* | 95 | 118 |
| B | Quench | Unit 3, 9/28, 1/10 Dil | 17588 | 78 | 84 | 97 | 87 | 95 | 80 |
| B | Quench | Unit 4, 9/28 | 17598 | 97 | 85 | 90 | 94 | 88 | 73 |
| B | Quench | Unit 4, 9/28, Dup | 17528 | 93 | 94 | 95 | 96* | 92 | 84 |
| B | Leachate | East Side | 19833 | 91 | 79 | 86 | 85 | 75 | 94 |
| B | Leachate | North Side | 19861 | 90 | 52 | 46 | 93 | 81 | 91 |
| B | Leachate | Northeast Corner | 19848 | 92 | 72 | 57 | 90 | 87 | 84 |
| C | Leachate | North Side | 19811 | 72 | 66 | 58 | 68 | 73 | 48 |
| C | Leachate | Northeast Corner | 19795 | 103 | 62 | 38 | 91 | 75 | 38 |
| C | Leachate | Northwest Corner | 19823 | 91 | 81 | 118 | 79 | 75 | 83 |
| C | MWell | #17 | 19781 | 87 | 77 | 119 | 82 | 84 | 44 |
| C | MWell | #3 | 19755 | 101 | 90 | 131 | 77 | 80 | 85 |
| C | MWell | #4 | 19768 | 95 | 86 | 129 | 70 | 71 | 72 |
| C | Quench | Unit 2, 9/30 | 19558 | 100 | 96 | 112 | 77 | 92 | 100 |
| C | Quench | Unit 2, 9/30 | 19558 MS | 99 | 96 | 111 | 77 | 82 | 93 |
| C | Quench | Unit 2, 9/30 | 19558 MSD | 105 | 103 | 112 | 82 | 86 | 97 |
| D | Leachate | Northeast Corner | 19628 | 81 | 65 | 36 | 37 | 28 | 93 |
| D | Leachate | Northeast Corner | 19615 | 28* | 61 | 8* | 47 | 33 | 103 |
| D | Leachate | Northeast Corner | 19618RE | 55 | 59 | 23* | 56 | 38 | 103 |
| D | Leachate | Southeast Corner | 19602 | 67 | 83 | 22* | 69 | 63 | 99 |
| D | Quench | Unit 2, 10/3 | 19641 | 76 | 30* | 14* | 89 | 79 | 34 |
| D | Quench | Unit 2, 10/3 | 19643RE | 64 | 25* | 26* | 71 | 74 | 18 |
| D | Quench | Unit 2, 10/3, Dup | 19653 | 88 | 29* | 19* | 104* | 91 | 45 |
| D | Quench | Unit 2, 10/3, Dup | 19656RE | 63 | 27* | 30* | 83 | 77 | 20 |
| D | Quench | Unit 2, 10/4 | 19694 | 68 | 31* | 9* | 104* | 100 | 35 |
| D | Quench | Unit 2, 10/4 | 19697RE | 72 | 25* | 0* | 73 | 69 | 0* |
| | Blank | Laboratory | RB587 | 74 | 84 | 101 | 43 | 61 | 61 |
| | Blank | Laboratory | RB587 | 88 | 90 | 112 | 72 | 70 | 59 |
| | Blank | Laboratory | RB599 | 72 | 76 | 115 | 72 | 76 | 69 |
| | Blank | Laboratory | RB686 | 96 | 94 | 108 | 90 | 99 | 79 |
| | | QC Limits | | 36-114 | 43-116 | 33-141 | 10-94 | 21-100 | 10-123 |

LEGEND:

MS - matrix spike sample  
MSD - matrix spike duplicate sample  
RE - sample was reextracted and analyzed  
* - value exceeds the QC limit

## TABLE 4.18 QC SUMMARY (INTERNAL) FOR ORGANIC ANALYSIS

### Surrogate Recoveries (%) for Laboratory Leachates (EP, TCLP, and SW-924)

| Facility | Sample Matrix | Leaching Procedure | Sample Number | Nitro Benzene-D5 | 2-Fluoro-Biphenyl | Terphenyl -D4 | Phenol -D5 | 2-Fluoro-Phenol | 2,4,6-Tribromo Phenol |
|---|---|---|---|---|---|---|---|---|---|
| A | Bottom/Fly | EP Toxicity | 17651 | 104 | 94 | 96 | 7* | 33 | 12 |
| A | Bottom/Fly | EP Toxicity | 17651MS | 109 | 98 | 103 | 55 | 31 | 20 |
| A | Bottom/Fly | EP Toxicity | 17651MSD | 107 | 90 | 98 | 78 | 84 | 71 |
| A | Bottom/Fly | EP Toxicity | 17651Dup | 105 | 95 | 99 | 76 | 84 | 70 |
| B | Fly | EP Toxicity | 17695 | 103 | 89 | 52 | 67 | 86 | 67 |
| B | Bottom | EP Toxicity | 17694 | 104 | 91 | 57 | 13 | 3* | 5* |
| C | Bottom/Fly | EP Toxicity | 19517 | 121* | 108 | 108 | 10 | 57 | 15 |
| C | Fly | EP Toxicity | 19521 | 92 | 96 | 97 | 29 | 4* | 6* |
| D | Fly | EP Toxicity | 19673 | 94 | 90 | 70 | 39 | 6* | 7* |
| D | Bottom/Fly | EP Toxicity | 19678 | 98 | 94 | 95 | 51 | 7* | 9* |
|  | Blank | NA | RB701 | 102 | 109 | 120 | 90 | 81 | 69 |
|  | Blank | NA | Blank | 63 | 68 | 60 | 74 | 83 | 73 |
| A | Bottom/Fly | TCLP | 17651 | 111 | 87 | 86 | 34 | 18* | 21 |
| A | Bottom/Fly | TCLP | 17651Dup | 90 | 90 | 84 | 81 | 50 | 66 |
| B | Bottom | TCLP | 17694 | 122* | 100 | 84 | 42 | 5* | 8* |
| C | Fly | TCLP | 19521 | 103 | 84 | 79 | 12 | 2* | 6* |
| D | Fly | TCLP | 19673 | 107 | 86 | 73 | 92 | 61 | 74 |
| D | Bottom/Fly | TCLP | 19678 | 109 | 86 | 82 | 66 | 10* | 18 |
|  | Blank | NA | RB701 | 102 | 109 | 120 | 90 | 81 | 69 |
|  | Blank | NA | Blank | 108 | 97 | 84 | 106* | 91 | 67 |
| C | Bottom/Fly | SW-924 | 19517 | 78 | 96 | 66 |  |  |  |
| D | Bottom/Fly | SW-924 | 19678#1 | 101 | 82 | 43 | 91 | 83 | 91 |
| D | Bottom/Fly | SW-924 | 19678#2 | 93 | 81 | 75 | 90 | 81 | 88 |
| D | Bottom/Fly | SW-924 | 19678MS | 105 | 89 | 83 | 85 | 80 | 91 |
| D | Bottom/Fly | SW-924 | 19678MSD | 114 | 92 | 86 | 86 | 81 | 86 |
|  | Blank | NA | RB712 | 89 | 78 | 87 | 88 | 88 | 89 |
|  |  | QC Limits |  | 36-114 | 43-116 | 33-141 | 10-94 | 21-100 | 10-123 |

LEGEND:

MS - matrix spike sample
MSD - matrix spike duplicate sample
RE - sample was reextracted and reanalyzed
* - value exceeds the QC limit

## TABLE 4.18 QC SUMMARY (INTERNAL) FOR ORGANIC ANALYSIS

### Matrix Spike Results for Field Water Samples (Precision and Accuracy)

| SPIKE COMPOUND | Facility C, Quench Water Sample No. 19558 | | | Facility C, Well Water Sample No. 19768 | | | QC Limits (%) | |
|---|---|---|---|---|---|---|---|---|
| Base/Neutral Extractables | MS | MSD | RPD | MS | MSD | RPD | RPD | Recovery |
| 1,2,4-Trichlorobenzene | 88 | 91 | 3 | 90 | 86 | 5 | 28 | 39-98 |
| Acenaphthene | 86 | 92 | 7 | 87 | 82 | 6 | 31 | 46-118 |
| 2,4-Dinitro Toluene | 77 | 80 | 4 | 119* | 107* | 19 | 38 | 24-96 |
| Pyrene | 84 | 88 | 5 | 120 | 116 | 3 | 31 | 26-127 |
| N-Nitroso-Di-n-Propylamine | 88 | 95 | 8 | 84 | 77 | 7 | 38 | 41-116 |
| 1,4-Dichlorobenzene | 83 | 86 | 4 | 82 | 76 | 8 | 28 | 36-97 |
| Acid Extractables | | | | | | | | |
| Pentachlorophenol | 81 | 83 | 2 | 58 | 57 | 2 | 50 | 9-103 |
| Phenol | 77 | 84 | 9 | 72 | 67 | 7 | 42 | 12-89 |
| 2-Chlorophenol | 79 | 83 | 5 | 72 | 67 | 7 | 40 | 27-123 |
| 4-Chloro-3-Methylphenol | 86 | 90 | 5 | 85 | 76 | 11 | 42 | 23-97 |
| 4-Nitrophenol | 23 | 18 | 24 | 76 | 69 | 10 | 50 | 10-80 |

### Matrix Spike Results for Laboratory Leachates (Precision and Accuracy)

| SPIKE COMPOUND | EP Toxicity Leachate Facility A, Bottom/Fly Sample No. 17651 | | | SW-924 Leachate Facility D, Bottom/Fly Sample No. 19678 Dup. | | | QC Limits (%) | |
|---|---|---|---|---|---|---|---|---|
| Base/Neutral Extractables | MS | MSD | RPD | MS | MSD | RPD | RPD | Recovery |
| 1,2,4-Trichlorobenzene | 82 | 83 | 1 | 77 | 79 | 3 | 28 | 39-98 |
| Acenaphthene | 84 | 83 | 1 | 78 | 79 | 1 | 31 | 46-118 |
| 2,4-Dinitro Toluene | 90 | 91 | 1 | 69 | 73 | 6 | 38 | 24-96 |
| Pyrene | 89 | 88 | 1 | 76 | 76 | 0 | 31 | 26-127 |
| N-Nitroso-Di-n-Propylamine | 88 | 89 | 1 | 84 | 90 | 7 | 38 | 41-116 |
| 1,4-Dichlorobenzene | 80 | 81 | 1 | 75 | 75 | 0 | 28 | 36-97 |
| Acid Extractables | | | | | | | | |
| Pentachlorophenol | 24 | 71 | 101* | 86 | 82 | 5 | 50 | 9-103 |
| Phenol | 51 | 72 | 34 | 93 | 91 | 2 | 42 | 12-89 |
| 2-Chlorophenol | 43 | 71 | 50* | 84 | 84 | 0 | 40 | 27-123 |
| 4-Chloro-3-Methylphenol | 88 | 88 | 1 | 84 | 85 | 1 | 42 | 23-97 |
| 4-Nitrophenol | 85 | 98 | 15 | 89 | 78 | 13 | 50 | 10-80 |

LEGEND:
MS = matrix spike sample
MSD = matrix spike duplicate sample
RPD = relative percent difference
* = value exceeds the QC limit

The criteria for recovery of surrogate compounds were generally achieved in the analyses of field water samples and laboratory-prepared leachates, with some exceptions. The Versar laboratory encountered difficulties with low recovery of the two heavier base neutral extractable compounds (2-fluoro biphenyl and terphenyl-D4) in analyses of leachates and quench water from Facility D. Four samples were re-extracted and reanalyzed with similar or poorer results indicating matrix interferences in the extraction and analysis. Problems with low recoveries were encountered also with the two heavier acid extractable surrogates (2-fluorophenol and 2,4,6-tribromophenol) in analyses of the EP and TCLP leachates. No acid extractable compounds were detected in the analyses of samples, however, so this problem is of no consequence.

The criteria for recoveries of Matrix Spike (MS) and Matrix Spike Duplicates (MSD), and for the Relative Percent Difference (RPD) between the two were generally achieved. No recoveries below the criteria were encountered. The precision (RPD) criteria of two of the acid extractable spikes (pentachlorophenol and 2-chlorophenol) in the analysis of the EP leachate of bottom/fly ash from Facility A were exceeded.

Overall, the analyses for BNAs in the field water samples and laboratory-prepared leachates were in control. The data from the analyses of samples are, therefore, considered valid. Corrective actions were taken by the laboratory on each occasion of a criteria exceedance in accordance with the Contract Laboratory Program protocol.

The total organic carbon (TOC) analyses and organic scans were also accompanied by internal quality control checks. These included analyses of reagent and calibration blanks, analyses of check standards, and analysis of an EPA quality control sample (WP-1248 for TOC and WP-379 for organic scan). The blanks were below the detection limits of the methods. Recoveries in analyses of the check standards and the EPA QC Standards ranged from 92 to 110 percent, within the QC criteria of 90 to 110 percent specified in the Quality Assurance Project Plan.

### 4.5.2 External QA/QC

The external QA/QC samples were field duplicate samples collected at a frequency of 25 percent. These samples were submitted to the laboratory as "blind" QC samples (i.e., the analysts were not aware that these samples were duplicates) to evaluate the precision of the entire sampling and analysis method. The analytical results of these external QA/QC samples are presented and evaluated in the following sections.

4.5.2.1 Metals - The results of the field duplicate analyses for metals and the relative percent differences (RPD) for these duplicate analyses are presented in Table 4.19. These results are summarized by sample matrix and facility.

A review of the bottom/fly or bottom ash field duplicate samples revealed the following. The precision for selenium and cadmium was the best, while iron, manganese, and zinc had the worst precision. The precision for Facility A was the best, followed by Facilities B, C, and D, sequentially. Finally, although the field duplicates had the increased variability of sampling, 17 of 44 sample parameter results had RPDs of <20 percent, which is the RPD criteria for duplicate metals analyses.

A review of the fly ash field duplicate samples showed the following. First, the precision for the manganese duplicate analyses was the best, and the precision for the cadmium duplicate analyses was the worst. The precision for Facility B was the best, followed by Facilities A, C, and D, sequentially. Finally, the RPD was <20 percent for 41 of 44 analyses. It was expected that the precision of the fly ash field duplicates would be better than the precision of the bottom/fly or bottom ash field duplicates because of the more homogeneous nature of the fly ash samples.

A review of the quench water field duplicate samples showed the following. First, the RPDs at Facility B were much better than those at Facility D. This was expected because of the quantity of floating solids

## TABLE 4.19 QC SUMMARY (EXTERNAL) FOR METALS

### TOTAL METALS IN SOLID SAMPLES

| Plant | Sample Matrix | Cd mg/kg | Cr mg/kg | Cu mg/kg | Fe mg/kg | Pb mg/kg | Mn mg/kg | Ni mg/kg | Zn mg/kg | As mg/kg | Se mg/kg | Hg mg/kg |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A | Bottom/Fly | 17 | 12 | 369 | 6650 | 2200 | 184 | 22 | 1730 | 7.9 | <5 | 6.9 |
| A | Bottom/Fly | 15 | 16 | 377 | 9140 | 1140 | 251 | 24 | 3050 | 12.2 | <5 | 5.0 |
|  | RPD (%) | 12.5% | 28.6% | 2.1% | 31.5% | 63.5% | 30.8% | 8.7% | 55.2% | 42.8% | 0.0% | 31.9% |
| C | Bottom/Fly | 24 | 19 | 3420 | 5040 | 1700 | 155 | 42 | 1570 | 5.7 | <5. | 0.62 |
| C | Bottom/Fly | 27 | 26 | 608 | 9720 | 1060 | 1810 | 38 | 3250 | 7 | <0.5 | 0.18 |
|  | RPD (%) | 11.8% | 31.1% | 139.6% | 63.4% | 46.4% | 168.4% | 10.0% | 69.7% | 20.5% | 163.6% | 110.0% |
| D | Bottom/Fly | 17 | 31 | 289 | 8590 | 571 | 3130 | 26 | 2400 | 5.4 | <1 | 0.21 |
| D | Bottom/Fly | 18 | 36 | 728 | 95100 | 612 | 640 | 119 | 46000 | 6.1 | <1 | 0.13 |
|  | RPD (%) | 5.7% | 14.9% | 86.3% | 166.9% | 6.9% | 132.1% | 128.3% | 180.2% | 12.2% | 0.0% | 47.1% |
| A | Fly | 193 | 79 | 2380 | 17400 | 5550 | 1010 | 106 | 15700 | 41.9 | <5 | 27 |
| A | Fly | 186 | 66 | 2040 | 15000 | 5400 | 1020 | 91 | 14500 | 38.0 | <5 | 23 |
|  | RPD (%) | 3.7% | 17.9% | 15.4% | 14.8% | 2.7% | 1.0% | 15.2% | 7.9% | 9.8% | 0.0% | 16.0% |
| B | Fly | 322 | 105 | 745 | 9900 | 7350 | 895 | 80 | 32700 | 106 | <10 | 9.3 |
| B | Fly | 316 | 98 | 724 | 9350 | 7270 | 889 | 76 | 31800 | 89.9 | <10 | 8.0 |
|  | RPD (%) | 1.9% | 6.9% | 2.9% | 5.7% | 1.1% | 0.7% | 5.1% | 2.8% | 16.4% | 0.0% | 15.0% |
| C | Fly | 191 | 54 | 531 | 8200 | 3490 | 388 | 102 | 10300 | 16.2 | 7.6 | 5 |
| C | Fly | 157 | 52 | 556 | 8450 | 3130 | 382 | 95 | 8460 | 17.7 | 6.2 | 4.0 |
|  | RPD (%) | 19.5% | 3.8% | 4.6% | 3.0% | 10.9% | 1.6% | 7.1% | 19.6% | 8.8% | 20.3% | 22.2% |
| D | Fly | 259 | 77 | 516 | 8320 | 5450 | 857 | 63 | 22100 | 50.7 | 9.6 | 1.8 |
| D | Fly | 172 | 67 | 518 | 7190 | 4600 | 751 | 55 | 18600 | 54.5 | 9.1 | 2.0 |
|  | RPD (%) | 40.4% | 13.9% | 0.4% | 14.6% | 16.9% | 13.2% | 13.6% | 17.2% | 7.2% | 5.3% | 10.5% |
| B | Bottom | 3.8 | 66 | 792 | 115000 | 2140 | 1010 | 36 | 2350 | 8.9 | <5. | 0.12 |
| B | Bottom | 3.5 | 78 | 581 | 24100 | 3930 | 938 | 90 | 5760 | 6.9 | <5. | 0.12 |
|  | RPD (%) | 8.2% | 16.7% | 30.7% | 130.7% | 59.0% | 7.4% | 85.7% | 84.1% | 25.3% | 0.0% | 0.0% |

# TABLE 4.19 QC SUMMARY (EXTERNAL) FOR METALS

## TOTAL METALS IN LIQUID SAMPLES

| Plant | Sample Matrix | Cd ug/L | Cr ug/L | Cu ug/L | Fe ug/L | Pb ug/L | Mn ug/L | Ni ug/L | Zn ug/L | As ug/L | Se ug/L | Hg ug/L |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| B | Quench | <5.0 | 8.5 | 48 | 409 | 274 | 82 | <18 | 218 | <10. | <25. | 1.0 |
| B | Quench | <5.0 | 8.5 | 41 | 348 | 264 | 79 | <18 | 203 | <10. | <25. | 0.99 |
| | RPD (%) | 0.0% | 0.0% | 15.7% | 16.1% | 3.7% | 3.7% | 0.0% | 7.1% | 0.0% | 0.0% | 1.0% |
| D | Quench | 795 | 408 | 2510 | 35000 | 19100 | 7470 | 190 | 64600 | 202 | <25. | 22 |
| D | Quench | 1300 | 646 | 3860 | 56200 | 27800 | 12600 | 322 | 132000 | 267 | <25. | 20 |
| | RPD (%) | 48.2% | 45.2% | 42.4% | 46.5% | 37.1% | 51.1% | 51.6% | 68.6% | 27.7% | 0.0% | 9.5% |

## EXTRACTABLE METALS IN LABORATORY LEACHATES

| Plant | Matrix (Leachate) | Cd mg/L | Cr mg/L | Cu mg/L | Fe mg/L | Pb mg/L | Mn mg/L | Ni mg/L | Zn mg/L | As mg/L | Se mg/L | Hg mg/L |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A | Fly | 6.02 | <0.005 | 0.045 | <0.005 | 4.72 | 6.62 | 0.326 | 186 | <0.01 | <0.05 | <0.008 |
| A | (EP Toxicity) | 7.72 | <0.005 | 0.254 | 0.007 | 10.8 | 8.03 | 0.466 | 262 | <0.01 | <0.05 | <0.008 |
| | RPD (%) | 24.7% | 0.0% | 139.8% | 94.7% | 78.4% | 19.2% | 35.4% | 33.9% | 0.0% | 0.0% | 0.0% |
| A | Fly | 0.015 | 0.136 | <0.005 | 190 | 0.962 | 4.62 | 0.372 | 77.6 | 0.024 | <0.025 | <0.008 |
| A | (TCLP) | 0.032 | <0.005 | 0.116 | <0.005 | <0.05 | 0.049 | <0.015 | 0.151 | <0.01 | <0.05 | <0.008 |
| | RPD (%) | 72.3% | 192.8% | 191.6% | 200.0% | 189.9% | 195.8% | 192.1% | 199.2% | 131.0% | 66.7% | 0.0% |
| A | Fly | <0.015 | 0.010 | 0.027 | 0.167 | <0.075 | 0.0058 | 0.0225 | 0.026 | <0.01 | <0.05 | <0.04 |
| A | (SW924-EX1) | <0.01 | <0.005 | 0.089 | <0.005 | <0.05 | 0.0017 | <0.015 | 0.045 | <0.01 | <0.005 | <0.02 |
| | RPD (%) | 40.0% | 120.0% | 106.9% | 194.1% | 40.0% | 109.3% | ERR | 53.5% | 0.0% | 163.6% | 66.7% |
| A | Fly | <0.01 | <0.005 | 0.009 | 0.057 | 0.072 | 0.003 | <0.015 | 0.083 | <0.01 | <0.005 | <0.02 |
| A | (SW924-EX2) | <0.01 | <0.005 | <0.005 | <0.005 | <0.05 | <0.001 | <0.015 | <0.003 | <0.01 | <0.005 | <0.02 |
| | RPD (%) | 0.0% | 0.0% | 113.0% | 183.2% | 96.9% | 142.9% | 0.0% | 192.9% | 0.0% | 0.0% | 0.0% |
| D | Fly | 8.60 | <0.005 | 0.041 | 0.012 | 1.96 | 6.74 | 0.288 | 430 | <0.01 | <0.05 | <0.008 |
| D | (EP Toxicity) | 9.18 | <0.005 | 0.131 | 0.0074 | 25.2 | 7.6 | 0.284 | 458 | <0.01 | <0.05 | <0.008 |
| | RPD (%) | 6.5% | 0.0% | 104.7% | 47.4% | 171.1% | 12.0% | 1.4% | 6.3% | 0.0% | 0.0% | 0.0% |

## TABLE 4.19 QC SUMMARY (EXTERNAL) FOR METALS

| Plant | Matrix (Leachate) | Cd mg/L | Cr mg/L | Cu mg/L | Fe mg/L | Pb mg/L | Mn mg/L | Ni mg/L | Zn mg/L | As mg/L | Se mg/L | Hg mg/L |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| D | Fly | 10.3 | 0.487 | 0.018 | 12.8 | 15.2 | 14.7 | 0.582 | 746 | 0.086 | <0.05 | <0.008 |
| D | (TCLP) | 8.90 | 0.544 | 0.0059 | 15.0 | 12.8 | 13.6 | 0.567 | 624 | 0.111 | <0.005 | <0.008 |
|  | RPD (%) | 14.6% | 11.1% | 101.3% | 15.8% | 17.1% | 7.8% | 2.6% | 17.8% | 25.4% | 163.6% | 0.0% |
| D | Fly | 0.015 | 0.071 | 0.0052 | <0.005 | <0.05 | 0.0061 | <0.015 | 0.180 | <0.01 | 0.047 | <0.02 |
| D | (SW924-EX1) | <0.01 | 0.114 | 0.0051 | <0.005 | <0.05 | <0.001 | 0.022 | 0.036 | <0.01 | <0.05 | <0.02 |
|  | RPD (%) | 100.0% | 46.5% | 1.9% | 0.0% | 0.0% | 169.7% | 98.3% | 133.3% | 0.0% | 61.1% | 0.0% |
| D | Fly | <0.01 | 0.116 | <0.005 | <0.005 | <0.05 | 0.002 | <0.015 | 0.018 | <0.01 | <0.025 | <0.02 |
| D | (SW924-EX2) | <0.01 | 0.15 | <0.005 | <0.005 | <0.05 | <0.001 | <0.015 | 0.02 | <0.01 | <0.025 | <0.02 |
|  | RPD (%) | 0.0% | 25.6% | 0.0% | 0.0% | 0.0% | 120.0% | 0.0% | 10.5% | 0.0% | 0.0% | 0.0% |

LEGEND:

EP TOX - EP TOXICITY extraction procedure
TCLP - TOTAL CHARACTERISTIC LEACHATE PROCEDURE
SW 924 - Procedure for estimating monofilled solid waste leachate composition
SW 924 EX1 - First extract using SW 924 procedure
SW 924 EX2 - Second extract (on the same sample) using SW 924 procedure
Fly - Fly ash
Bottom/Fly - Combined bottom ash and fly ash
Bottom - Bottom ash
Quench - Quench water
RPD - Relative Percent Difference

in the quench water from Facility D. Second, the RPDs for selenium and mercury analyses were the best, while the RPDs for copper, iron, and zinc were the worst. Finally, the RPD was <20 percent for 13 of 22 analyses.

A review of the laboratory leachate field duplicate samples revealed the following. First, the precision of the EP method was good for cadmium, chromium, manganese, arsenic, selenium, and mercury and was poor for copper, iron, and lead. The RPD was <20 percent for 13 of the 22 EP leachate duplicate parameters. Second, the precision for the EP method was much better than for the TCLP and MWEP (SW924) methods. The RPD was <20 percent for 11 of 22 TCLP duplicate parameters. Finally, for the MWEP method, only two out of 21 sample parameters which were detected had an RPD of <20 percent.

Overall, the quality control results for metals based on the differences between duplicate samples did not suggest the presence of a significant systematic error. Some random errors are inevitable in a measurement (sampling and analysis) process. The random anomalies that did occur with the metals data were isolated and did not affect subsequent interpretations of the data.

4.5.2.2 PCBs - The results of the duplicate analyses of selected samples for individual PCB homologs and total PCBs are summarized by sample matrix and facility and presented in Table 4.20.

A review of the results for fly ash field duplicate samples revealed the following. The RPD increased as the level of chlorination increased. The RPD ranged from 0.0 percent to 45.5 percent for total PCBs and from 0.0 percent to 81.0 percent for individual PCB homologs.

A review of the results for the analysis of combined ash and bottom ash field duplicate samples provided minimal information because no PCBs were detected in field duplicate samples from Facilities A, B, and C. However, the RPDs for the combined ash from Facility D ranged from 100 percent to 134.7 percent for the individual PCB homologs, and the RPD

## TABLE 4.20 QC SUMMARY (EXTERNAL) FOR PCB ANALYSIS

### QC RESULTS FOR SOLIDS

| Plant | Sample Matrix | MONO -CB (ng/g) | DI -CB (ng/g) | TRI -CB (ng/g) | TETRA -CB (ng/g) | PENTA -CB (ng/g) | TOTAL PCB (ng/g) |
|---|---|---|---|---|---|---|---|
| A | Fly Ash | | 0.70 | | | | 0.70 |
| A | Fly Ash | | 0.73 | | | | 0.73 |
| | RPD (%) | | 4.2% | | | | 4.2% |
| A | Bottom/Fly | | | | | | ND |
| A | Bottom/Fly | | | | | | ND |
| | RPD (%) | | | | | | 0.0% |
| B | Fly Ash | | | | | | ND |
| B | Fly Ash | | | | | | ND |
| | RPD (%) | | | | | | 0.0% |
| B | Bottom | | | | | | ND |
| B | Bottom | | | | | | ND |
| | RPD (%) | | | | | | 0.0% |
| C | Fly Ash | | <0.20 | | | | <0.20 |
| C | Fly Ash | | 0.81 | | | | 0.81 |
| | RPD (%) | | 156.0% | | | | 156.0% |
| C | Bottom/Fly | | | | | | ND |
| C | Bottom/Fly | | | | | | ND |
| | RPD (%) | | | | | | 0.0% |
| D | Fly Ash | | 2.88 | 2.91 | 2.41 | | 8.20 |
| D | Fly Ash | | 2.42 | 1.72 | 1.02 | | 5.16 |
| | RPD (%) | | 17.4% | 51.4% | 81.0% | | 45.5% |
| D | Bottom/Fly | | <0.20 | 2.79 | <0.20 | | 2.79 |
| D | Bottom/Fly | | 1.35 | 14.3 | 16.5 | | 32.15 |
| | RPD (%) | | 172.4% | 134.7% | 197.6% | | 168.1% |

## TABLE 4.20 QC SUMMARY (EXTERNAL) FOR PCB ANALYSIS

### QC RESULTS FOR LIQUIDS

| Sample Plant | Description | MONO -CB ug/L | DI -CB ug/L | TRI -CB ug/L | TETRA -CB ug/L | PENTA -CB ug/L | TOTAL PCB ug/L |
|---|---|---|---|---|---|---|---|
| D | Field Leachate | | | | | | ND |
| D | Field Leachate | | | | | | ND |
| | RPD (%) | | | | | | 0.0% |
| B | Quench Water | 0.002 | | | | | 0.002 |
| B | Quench Water | 0.03 | | | | | 0.03 |
| | RPD (%) | 175.0% | | | | | 175.0% |
| D | Quench Water | | | | | | ND |
| D | Quench Water | | | | | | ND |
| | RPD (%) | | | | | | 0.0% |

LEGEND:

MONO -CB = Monochlorinated Biphenyl
DI -CB = Dichlorinated Biphenyl
TRI -CB = Trichlorinated Biphenyl
TETRA -CB = Tetrachlorinated Biphenyl
PENTA -CB = Pentachlorinated Biphenyl
ND = Not Detected

for the total PCBs was 168.1 percent. This large RPD may be attributed to the heterogeneous nature of the combined ash samples.

A review of results from the analysis field water duplicate samples showed that for a majority of the duplicates no conclusions of the precision could be made because of the extremely low concentrations of PCBs.

4.5.2.3 PCDD/PCDFs - The results of the duplicate analyses for individual and total PCDD and PCDF homologs is presented in Table 4.21. These results are summarized by sample matrix and facility.

A review of the fly ash data for PCDD/PCDF field duplicate sample analyses revealed the following. First, 19 of 24 PCDD and 14 of 20 PCDF duplicates had an RPD of <20 percent. Second, the precision of the PCDDs was slightly better than that of the PCDFs. Third, the RPDs increased as the concentrations of the individual homologs increased. Fourth, the PCDD precision was best for Facilities C and D, while the PCDF precision was best for Facilities A and B. Finally, the precision for the tetra-chlorinated classes of both PCDD and PCDF were best, while the precision of the hepta-chlorinated classes of both PCDD and PCDF were worst.

The results from the combined ash and bottom ash field duplicate sample analyses showed the following. First, 5 of 12 PCDD and 1 of 12 PCDF duplicate results had an RPD of less than 20 percent. This decreased precision among the combined/bottom ash duplicates is a result of the heterogeneity of the samples. Second, the precision for the PCDDs was slightly better than for the PCDFs. Third, the RPDs decreased as the concentrations of the individual homologs increased. Fourth, both the PCDD and PCDF precision was better for Facility C than for Facility B. This may be a result of the Facility C duplicate samples being combined bottom/fly ash, while the Facility B duplicate samples were exclusively the more heterogeneous bottom ash. Finally, the precision was best for the octa-CDD and octa-CDF homologs and was worst for the penta-CDD and hepta-CDF homologs.

## TABLE 4.21 QC SUMMARY (EXTERNAL) FOR PCDD/PCDF ANALYSIS

### QC RESULTS FOR SOLIDS (DIOXIN HOMOLOGS)

| Plant | Sample Matrix | 2,3,7,8 TCDD ng/g | TETRA -CDD ng/g | PENTA -CDD ng/g | HEXA -CDD ng/g | HEPTA -CDD ng/g | OCTA -CDD ng/g | TOTAL -CDD ng/g |
|---|---|---|---|---|---|---|---|---|
| A | Fly Ash | 0.093 | 2.3 | 11 | 20 | 14 | 17 | 64.3 |
| A | Fly Ash | 0.11 | 2.8 | 14 | 20 | 14 | 18 | 68.8 |
| | RPD | 16.7% | 19.6% | 24.0% | 0.0% | 0.0% | 5.7% | 6.8% |
| B | Fly Ash | 0.38 | 12 | 139 | 126 | 100 | 96 | 473 |
| B | Fly Ash | 0.38 | 11 | 114 | 123 | 93 | 89 | 430 |
| | RPD | 0.0% | 8.7% | 19.8% | 2.4% | 7.3% | 7.6% | 9.5% |
| B | Bottom Ash | <0.08 | <0.08 | <0.05 | 0.07 | 0.13 | 0.35 | 0.55 |
| B | Bottom Ash | 0.01 | 0.11 | 0.21 | 0.16 | 0.24 | 0.61 | 1.33 |
| | RPD | 120.0% | 93.3% | 157.4% | 78.3% | 59.5% | 54.2% | 83.0% |
| C | Fly Ash | 1.5 | 31 | 710 | 5565 | 1759 | 2460 | 10525 |
| C | Fly Ash | 2.1 | 33 | 722 | 3946 | 3030 | 3152 | 10883 |
| | RPD | 33.3% | 6.3% | 1.7% | 34.0% | 53.1% | 24.7% | 3.3% |
| C | Bottom/Fly | 0.62 | 14 | 47 | 67 | 120 | 89 | 337 |
| C | Bottom/Fly | 0.78 | 13 | 50 | 78 | 120 | 89 | 350 |
| | RPD | 22.9% | 7.4% | 6.2% | 15.2% | 0.0% | 0.0% | 3.8% |
| D | Fly Ash | 0.38 | 5.2 | 54 | 105 | 45 | 44 | 253.2 |
| D | Fly Ash | 0.45 | 5.1 | 46 | 103 | 48 | 48 | 250.1 |
| | RPD | 16.9% | 1.9% | 16.0% | 1.9% | 6.5% | 8.7% | 1.2% |

## TABLE 4.21 QC SUMMARY (EXTERNAL) FOR PCDD/PCDF ANALYSIS

### QC RESULTS FOR SOLIDS (FURAN HOMOLOGS)

| Fac. | Sample Matrix | 2,3,7,8 TCDF ng/g | TETRA -CDF ng/g | PENTA -CDF ng/g | HEXA -CDF ng/g | HEPTA -CDF ng/g | OCTA -CDF ng/g | TOTAL -CDF ng/g | PCDD + PCDF ng/g |
|---|---|---|---|---|---|---|---|---|---|
| A | Fly Ash | | 20 | 7.1 | 17 | 14 | 2.1 | 60.2 | 124.5 |
| A | Fly Ash | | 23 | 10 | 14 | 12 | 2.3 | 61.3 | 130.1 |
| | RPD | | 14.0% | 33.9% | 19.4% | 15.4% | 9.1% | 1.8% | 4.4% |
| B | Fly Ash | | 91 | 64 | 56 | 40 | 8.1 | 259.1 | 732.1 |
| B | Fly Ash | | 97 | 65 | 61 | 40 | 8.3 | 271.3 | 701.3 |
| | RPD | | 6.4% | 1.6% | 8.5% | 0.0% | 2.4% | 4.6% | 4.3% |
| B | Bottom Ash | 0.05 | 0.28 | 0.18 | 0.1 | 0.1 | 0.06 | 0.72 | 1.27 |
| B | Bottom Ash | 0.09 | 0.68 | 0.33 | 0.26 | 0.26 | 0.12 | 1.65 | 2.98 |
| | RPD | 57.1% | 83.3% | 58.8% | 88.9% | 88.9% | 66.7% | 78.5% | 80.5% |
| C | Fly Ash | | 164 | 221 | 336 | 32 | 60 | 813 | 11338 |
| C | Fly Ash | | 169 | 226 | 2353 | 77 | 362 | 3187 | 14070 |
| | RPD | | 3.0% | 2.2% | 150.0% | 82.6% | 143.1% | 118.7% | 21.5% |
| C | Bottom/Fly | 2.9 | 20 | 20 | 24 | 27 | 6.7 | 97.7 | 434.7 |
| C | Bottom/Fly | 3.8 | 24 | 27 | 35 | 36 | 8.4 | 130.4 | 480.4 |
| | RPD | 26.9% | 18.2% | 29.8% | 37.3% | 28.6% | 22.5% | 28.7% | 10.0% |
| D | Fly Ash | | 36 | 32 | 115 | 80 | 4.9 | 267.9 | 521.1 |
| D | Fly Ash | | 36 | 27 | 21 | 3.8 | 5.6 | 93.4 | 343.5 |
| | RPD | | 0.0% | 16.9% | 138.2% | 181.9% | 13.3% | 96.6% | 41.1% |

## TABLE 4.21 QC SUMMARY (EXTERNAL) FOR PCDD/PCDF ANALYSIS

### QC RESULTS FOR LIQUIDS (DIOXIN HOMOLOGS)

| Plant | Sample Matrix | 2,3,7,8 TCDD (ng/l) | TETRA -CDD (ng/l) | PENTA -CDD (ng/l) | HEXA -CDD (ng/l) | HEPTA -CDD (ng/l) | OCTA -CDD (ng/l) | TOTAL -CDD (ng/l) |
|---|---|---|---|---|---|---|---|---|
| D | Field Leachate | <0.22 | 0.13 | 0.4 | 2.2 | 8.2 | 23 | 33.93 |
| D | Field Leachate | <0.26 | 0.27 | <0.22 | 2.1 | 8.8 | 25 | 36.17 |
| | RPD | 16.7% | 70.0% | 113.7% | 4.7% | 7.1% | 8.3% | 6.4% |
| B | Quench Water | <0.07 | <0.07 | <0.03 | <0.01 | <0.03 | 0.06 | 0.06 |
| B | Quench Water | <0.07 | <0.07 | <0.05 | <0.04 | 0.05 | 0.13 | 0.18 |
| | RPD | 0.0% | 0.0% | 50.0% | 125.9% | 107.7% | 73.7% | 100.0% |
| D | Quench Water | 8.2 | 190 | 610 | 500 | 450 | 250 | 2000 |
| D | Quench Water | 17 | 700 | 650 | 450 | 420 | 330 | 2550 |
| | RPD | 69.8% | 114.6% | 6.3% | 10.5% | 6.9% | 27.6% | 24.2% |

### QC RESULTS FOR LIQUIDS (FURAN HOMOLOGS)

| Plant | Sample Matrix | 2,3,7,8 TCDF (ng/l) | TETRA -CDF (ng/l) | PENTA -CDF (ng/l) | HEXA -CDF (ng/l) | HEPTA -CDF (ng/l) | OCTA -CDF (ng/l) | TOTAL -CDF (ng/l) | TCDD + TCDF (ng/l) |
|---|---|---|---|---|---|---|---|---|---|
| D | Field Leachate | 0.37 | 3 | 2.3 | 1.9 | 1.3 | 0.84 | 9.34 | 43.27 |
| D | Field Leachate | 0.4 | 2.9 | 2.4 | 1.9 | 1.2 | 0.81 | 9.21 | 45.38 |
| | RPD | 7.8% | 3.4% | 4.3% | 0.0% | 8.0% | 3.6% | 1.4% | 4.8% |
| B | Quench Water | <0.06 | <0.06 | <0.01 | <0.01 | <0.02 | <0.15 | 0 | 0.06 |
| B | Quench Water | <0.08 | <0.08 | <0.04 | <0.02 | 0.04 | <0.30 | 0.04 | 0.22 |
| | RPD | 28.6% | 28.6% | 120.0% | 66.7% | 120.0% | 66.7% | 200.0% | 114.3% |
| D | Quench Water | 110 | 640 | 560 | 490 | 310 | 75 | 2075 | 4075 |
| D | Quench Water | 99 | 590 | 460 | 390 | 280 | 68 | 1788 | 4338 |
| | RPD | 10.5% | 8.1% | 19.6% | 22.7% | 10.2% | 9.8% | 14.9% | 6.3% |

LEGEND:

Bottom/Fly = Combined bottom ash and fly ash
PCDD = Polychlorinated dibenzodioxins
PCDF = Polychlorinated dibenzofurans
RPD = relative percent difference

The results for the field leachate and quench water field duplicate samples analyses showed the following. First, 9 of 18 PCDD and 10 of 18 PCDF duplicate results had an RPD of less than 20 percent. Second, the precision was better for the PCDFs than for the PCDDs. Third, the precision was also better for the field leachates than for the quench water samples, which was expected because the quench water samples contained floating solids that added to their heterogeneity. However, these results are misleading because the PCDD and PCDF concentrations were near the detection limits, which make the RPDs unrepresentatively high. Finally, the precision was best for the octa-CDD and tetra-CDF homologs, and was worst for the tetra-CDD and penta-CDF homologs.

Overall, the quality of the PCDD/PCDF data appeared to be excellent therefore suggesting that the data could be used with a high degree of confidence.

4.5.2.4 Organic Constituents - The results of the duplicate analyses for organic constituents are presented in Table 4.22. This table shows that the precision is generally good. Relative percent differences were not calculated because of the nature of the analysis and the multitude of BNA compounds which were tentatively identified. Therefore, any calculation of RPDs would not be representative of the actual sampling and analysis precision, due to the nature of the analytical method.

## TABLE 4.22 QC SUMMARY (EXTERNAL) FOR ORGANICS

| Plant | Sample Description | TOC (mg/l) | Organic Scan (mg/l) | BNA Peaks Found (No.) | Ethyl Hexyl Phthalate 117817 (ug/L) | Dimethyl Propane Diol 126307 (ug/L) | Biphenyl 90437 (ug/L) | Hexa Thiepane 17233715 (ug/L) | Thiolane 289167 (ug/L) | Unknown HCs (#) | Unknowns (#) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| D | Field Leacha | 636.0 | <0.25 | 22 | 80 | 110 | 51 | 82 | 400 | 9 | 8 |
| D | Field Leacha | 567.0 |  | 24 | 37 | 120 | 51 |  | 140 | 10 | 10 |

| Plant | Sample Matrix | TOC (mg/l) | Organic Scan (mg/l) | BNA Peaks Found (No.) | Phenol 108952 (ug/L) | 2-Methyl phenol 95487 (ug/L) | 4-Methyl phenol 106445 (ug/L) | Benzoic Acid 65850 (ug/L) | Molecular Sulfur 10544500 (ug/L) | Thiolane 289167 (ug/L) | 2-Hydroxy Benzoic Acid 69727 (ug/L) | Hexanoic Acid 142621 (ug/L) | Unknowns (#) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| B | Quench Water | 421.0 | <0.25 | 20 | 380 | 40 | 92 | 2100 | 29 |  | 50 | 58 | 13 |
| B | Quench Water | 416.5 | <0.25 | 20 | 380 | 44 | 94 | 2100 | 130 | 23 | 42 | 37 | 12 |

| Plant | Sample Matrix | TOC (mg/l) | Organic Scan (mg/l) | BNA Peaks Found (No.) | Phenol 108952 (ug/L) | 2-Methyl phenol 95487 (ug/L) | 4-Methyl phenol 106445 (ug/L) | Benzoic Acid 65850 (ug/L) | Hexyl Phthalate 117817 (ug/L) | Hexanoic Acid 142621 (ug/L) | Methyl Pentanoic Acid 646071 (ug/L) | Benz-aldehyde 100527 (ug/L) | Methyl Pentane-diol 144194 (ug/L) | Furan Carbox-aldehyde 67470 (ug/L) | Benzene Propanoic Acid 501520 (ug/L) | Tetra Decanoic Acid 544638 (ug/L) | Methyl Purine Dione 58082 (ug/L) | Unknown Org Acids (#) | Unknown HCs (#) | Unknowns (#) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| D | Quench Water | 165.0 | <0.25 | 25 | 60 | 7 | 23 | 570 | 8 | 45 | 17 | 22 | 17 | 54 | 23 | 72 | 23 | 1 | 2 | 9 |
| D | Quench Water | 153.0 |  | 25 | 71 | 7 |  | 900 |  | 51 | 84 |  |  |  | 12 |  | 22 | 1 |  | 17 |

## 5.0 EVALUATION

In this section, the data presented and discussed in Section 4.0 are summarized and evaluated. To facilitate this evaluation, the data were averaged by facility, sample type, and analytical parameter combinations. Then, the data were evaluated with respect to previously reported information, variations between sample types, variations between laboratory leachate preparation procedures, municipal waste combustor (MWC) facility design and operation, and characterization of the residues as hazardous wastes. Section 5.1 presents the concentration ranges for each sample type and analytical parameter from this study and compares them to the concentration ranges from previous studies. Section 5.2 presents the data summary tables and an evaluation of the significant trends observed from these tables. Section 5.3 provides a qualitative evaluation of the relationships between MWC facility design and operating characteristics and the concentrations of constituents in the residues. Finally, Section 5.4 presents an overall assessment of the hazardous waste characteristics of the MWC residues based on existing standards and criteria.

### 5.1 Comparative Evaluation With Previously Reported Information

The data extracted from the documents identified in the literature review (see Section 2.0) were summarized by sample type and analytical parameter. From the summarized data, a concentration range was determined for each sample type/analytical parameter combination from the previous studies. The lower end of any given range was the minimum concentration reported in any previous study for that particular sample type/analytical parameter combination. Similarly, the upper end of any given range was the maximum concentration reported in any previous study for that particular sample type/analytical parameter combination. Using an analagous approach, the concentration range was determined for each sample type/analytical parameter combination from this study. However, previous studies did not provide any data for PCDD/PCDFs or organic constituents (i.e., BNAs) in laboratory-prepared leachates, or for PCBs or PCDD/PCDFs in field water samples (i.e., quench water, field leachate, and ground water). Sections 5.1.1 through 5.1.3 present the concentration ranges from this study and from previous studies for the available sample type/analytical parameter combinations and provide a narrative evaluation of the findings.

### 5.1.1 Solid Samples

The concentration ranges for metals in fly ash and combined ash are presented in Table 5.1. As can be seen from this table, the results for the fly ash from this study are within the concentration ranges from previous studies for all metals except copper, mercury, and selenium, where Versar's results are slightly higher. Similarly, for the combined ash, the results from this study are within the concentration ranges from previous studies for all metals except copper and zinc. One possible explanation for these discrepancies may be that in several of the previous studies, only one MWC facility was sampled, and the concentration range arising from the sampling, analytical, and operational variability at one facility would not be expected to encompass the concentration range resulting from four different facilities. Generally, the results for both the fly ash and combined ash from this study extend from the low end to the midpoint of the range from the previous studies.

The concentration ranges for PCBs in fly ash and combined ash are presented in Table 5.2. Both the fly ash and combined ash results from this study are within the concentration ranges from previous studies for every individual PCB homolog, as well as for total PCBs. Generally, the results from this study are near the lower end of the ranges from the previous studies for both ash types. One noteworthy trend is that the higher chlorinated species of PCBs (i.e., the hepta- through deca-chlorinated species) were not detected either in this study or in the previous studies, except for negligible concentrations of hepta-CB and octa-CB in the fly ash.

## TABLE 5.1 COMPARATIVE EVALUATION OF TOTAL METALS IN SOLID SAMPLES

### FLY ASH

| Metal | Concentration Range From This Study (mg/kg) | Concentration Range From Previous Studies (mg/kg) | References [1] |
|---|---|---|---|
| Arsenic (As) | 16 - 149 | 4.8 - 750 | 42, 53 |
| Cadmium (Cd) | 107 - 475 | 5.0 - 2,210 | 34, 42 |
| Chromium (Cr) | 48 - 105 | 21 - 1,900 | 34, 53 |
| Copper (Cu) | 484 - 2,380 | 187 - 2,300 | 53 |
| Iron (Fe) | 5,960 - 22,300 | 900 - 87,000 | 34, 53 |
| Lead (Pb) | 2,830 - 14,400 | 200 - 26,600 | 30, 42, 53 |
| Manganese (Mn) | 320 - 1,410 | 171 - 8,500 | 34, 53 |
| Mercury (Hg) | 0.94 - 35.0 | ND(0.02) - 6.77 | 30, 53 |
| Nickel (Ni) | 52 - 245 | ND(1.5) - 3,600 | 46 |
| Selenium (Se) | ND(5) - 15.6 | ND(0.2) - 12 | 30 |
| Zinc (Zn) | 8,460 - 38,800 | 2,800 - 152,000 | 30, 42, 53 |

### COMBINED ASH [2]

| Metal | Concentration Range From This Study (mg/kg) | Concentration Range From Previous Studies (mg/kg) | References [1] |
|---|---|---|---|
| Arsenic (As) | 2.2 - 24.6 | 0.8 - 50 | 53 |
| Cadmium (Cd) | 1.1 - 45.0 | 0.18 - 100 | 53 |
| Chromium (Cr) | 12 - 332 | 13 - 1,500 | 30, 42, 53 |
| Copper (Cu) | 193 - 10,700 | 40 - 3,400 | 53 |
| Iron (Fe) | 2,100 - 115,000 | 690 - 133,500 | 53 |
| Lead (Pb) | 259 - 13,200 | 31 - 36,600 | 53 |
| Manganese (Mn) | 110 - 3,130 | 14 - 4,800 | 46, 53 |
| Mercury (Hg) | 0.11 - 8.7 | ND(0.02) - 17.5 | 30, 53 |
| Nickel (Ni) | 13 - 556 | ND(1.5) - 12,910 | 46, 53 |
| Selenium (Se) | ND(0.5) - 1.4 | ND(0.2) - 50 | 53 |
| Zinc (Zn) | 545 - 46,000 | 92 - 7,000 | 46, 53 |

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ND - Not Detected; the detection limit is given in parentheses following ND.

[1] - The number(s) in the reference column corresponds to the reference item number in Appendix A from which the concentration range from previous studies was extracted.

[2] - The concentration ranges were derived from both combined bottom/fly and discrete bottom ash samples.

# TABLE 5.2 COMPARATIVE EVALUATION OF PCBs IN SOLID SAMPLES

## FLY ASH

| PCB Homolog | Concentration Range From This Study (ng/g) | Concentration Range From Previous Studies (ng/g) | References [1] |
|---|---|---|---|
| Mono-CB | ND(0.1) - 1.46 | ND(0.01) - 9.7 | 35, 76 |
| Di-CB | ND(0.1) - 7.87 | ND(0.1) - 10 | 35, 76 |
| Tri-CB | ND(0.1) - 7.67 | ND(0.1) - 25 | 76 |
| Tetra-CB | ND(0.1) - 5.52 | 0.5 - 470 | 35, 76 |
| Penta-CB | ND(0.1) - 2.25 | ND(0.1) - 130 | 35, 76 |
| Hexa-CB | ND(0.1) | ND(0.1) - 55 | 35, 76 |
| Hepta-CB | ND(0.1) | ND(0.01) - 0.2 | 35, 76 |
| Octa-CB | ND(0.1) | ND(0.01) - 2.5 | 35, 76 |
| Nona-CB | ND(0.1) | ND(0.01) | 35 |
| Deca-CB | ND(0.1) | ND(0.01) | 35 |
| TOTAL PCBs | ND(0.1) - 24.8 | ND(0.1) - 250 | 30, 35, 76 |

## COMBINED ASH [2]

| PCB Homolog | Concentration Range From This Study (ng/g) | Concentration Range From Previous Studies (ng/g) | References [1] |
|---|---|---|---|
| Mono-CB | ND(0.1) | ND(0.01) - 1.4 | 35, 76 |
| Di-CB | ND(0.1) - 1.35 | ND(0.1) - 5.5 | 35, 76 |
| Tri-CB | ND(0.1) - 14.3 | ND(0.1) - 80 | 35, 76 |
| Tetra-CB | ND(0.1) - 16.5 | ND(0.1) - 47 | 35, 76 |
| Penta-CB | ND(0.1) | ND(0.1) - 48 | 35, 76 |
| Hexa-CB | ND(0.1) | ND(0.1) - 39 | 35, 76 |
| Hepta-CB | ND(0.1) | ND(0.01) | 76 |
| Octa-CB | ND(0.1) | ND(0.01) | 76 |
| Nona-CB | ND(0.1) | ND(0.1) | 35 |
| Deca-CB | ND(0.1) | ND(0.1) | 35 |
| TOTAL PCBs | ND(0.1) - 32.2 | ND(0.1) - 180 | 30, 76 |

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ND - Not Detected; the detection limit is given in parentheses following ND.

[1] - The number(s) in the reference column corresponds to the reference item number in Appendix A from which the concentration range from previous studies was extracted.

[2] - The concentration ranges were derived from both combined bottom/fly and discrete bottom ash samples.

The concentration ranges for PCDDs and PCDFs in fly ash and combined ash are presented in Table 5.3. This table shows that both the fly ash and combined ash results for PCDDs and PCDFs generally exceed the concentration ranges from the previous studies, particularly for the highly chlorinated species of both PCDDs and PCDFs (i.e., the hexa- through octa-chlorinated species of both PCDDs and PCDFs). These exceedances are more pronounced for the PCDDs than for the PCDFs. Similarly, they are more pronounced for the fly ash than for the combined ash. These discrepancies may again be explained by the lack of a complete data base from previous studies.

### 5.1.2 Laboratory Leachates

Table 5.4 presents the concentration ranges for metals in the EP (extraction procedure toxicity) leachates prepared from fly ash and combined ash samples. The results for the EP-prepared fly ash leachates from this study are within the concentration ranges from previous studies, except for iron and manganese, where slightly higher results were found by Versar. Similarly, the results for the EP-prepared combined ash leachates from this study are within the concentration ranges from previous studies for all metals except copper, iron, lead, and zinc. As was the case for the solid samples, these slight discrepancies may be attributed to the concentration ranges which were extracted from one previous study of only one MWC facility.

The concentration ranges for metals in the TCLP (toxicity characteristic leaching procedure) leachates prepared from fly ash and combined ash samples are given in Table 5.5. Although the cadmium, copper, lead, and nickel results from the Versar study are within the concentration ranges from the previous studies, the results for the TCLP-prepared fly ash leachates from this study are generally higher than the upper end of the ranges from the previous studies. Similarly, the results for the TCLP-prepared combined ash leachates from this study exceeded the upper end of the ranges from previous studies for cadmium, chromium, manganese,

## TABLE 5.3 COMPARATIVE EVALUATION OF PCDD/PCDFs IN SOLID SAMPLES

### FLY ASH

| PCDD/PCDF Homolog | Concentration Range From This Study (ng/g) | Concentration Range From Previous Studies (ng/g) | References [1] |
|---|---|---|---|
| 2,3,7,8-TCDD | 0.11 - 3.9 | ND(0.1) - 42 | 30, 76 |
| Tetra-CDD | 2.3 - 43 | 2.4 - 250 | 76 |
| Penta-CDD | 11 - 722 | 0.5 - 650 | 35, 76 |
| Hexa-CDD | 18 - 5,565 | 0.2 - 2,496 | 12, 76 |
| Hepta-CDD | 14 - 3,030 | ND(0.1) - 410 | 76 |
| Octa-CDD | 11 - 3,152 | ND(0.1) - 841.5 | 12, 76 |
| TOTAL PCDDs | 64.3 - 10,883 | ND(0.1) - 4,700 | 12, 30, 35, 76 |
| 2,3,7,8-TCDF | N.A. | ND(0.1) - 5.4 | 76 |
| Tetra-CDF | 20 - 169 | 0.4 - 460 | 35, 76 |
| Penta-CDF | 7.1 - 226 | ND(0.1) - 1,800 | 35, 76 |
| Hexa-CDF | 14 - 2,353 | ND(0.1) - 1,100 | 76 |
| Hepta-CDF | 3.8 - 666 | ND(0.1) - 500 | 76 |
| Octa-CDF | 1.4 - 362 | ND(0.1) - 255 | 12, 76 |
| TOTAL PCDFs | 60.2 - 3,187 | ND(0.1) - 3,000 | 30, 76 |
| TOTAL PCDD/PCDFs | 124.5 - 14,070 | ND(0.1) - 7,700 | 12, 30, 35, 76 |

### COMBINED ASH [2]

| PCDD/PCDF Homolog | Concentration Range From This Study (ng/g) | Concentration Range From Previous Studies (ng/g) | References [1] |
|---|---|---|---|
| 2,3,7,8-TCDD | ND(0.1) - 0.78 | 0.2 - 6.7 | 76 |
| Tetra-CDD | ND(0.1) - 14 | 0.13 - 92 | 76 |
| Penta-CDD | ND(0.1) - 50 | ND(0.1) - 13 | 35, 76 |
| Hexa-CDD | ND(0.1) - 78 | ND(0.1) - 9.0 | 35, 76 |
| Hepta-CDD | ND(0.1) - 120 | ND(0.1) - 1.7 | 35, 76 |
| Octa-CDD | 0.16 - 89 | ND(0.1) | 35, 76 |
| TOTAL PCDDs | 0.27 - 350 | ND(0.1) - 110 | 30, 35, 76 |

TABLE 5.3 (CONTINUED)

COMBINED ASH [2]

| PCDD/PCDF Homolog | Concentration Range From This Study (ng/g) | Concentration Range From Previous Studies (ng/g) | References [1] |
|---|---|---|---|
| 2,3,7,8-TCDF | ND(0.1) - 12 | 0.2 - 1.3 | 76 |
| Tetra-CDF | ND(0.1) - 91 | ND(0.1) - 8.4 | 76 |
| Penta-CDF | ND(0.1) - 37 | ND(0.1) - 12 | 76 |
| Hexa-CDF | ND(0.1) - 35 | ND(0.1) - 2.5 | 35, 76 |
| Hepta-CDF | ND(0.1) - 36 | ND(0.1) - 0.8 | 35, 76 |
| Octa-CDF | ND(0.1) - 8.4 | ND(0.1) - 0.9 | 35, 76 |
| TOTAL PCDFs | 0.16 - 153.9 | ND(0.1) - 65 | 30, 35, 76 |
| TOTAL PCDD/PCDFs | 0.48 - 480.4 | ND(0.1) - 175 | 30, 35, 76 |

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N.A.- Not Available

ND - Not Detected; the detection limit is given in parentheses following ND.

[1] - The number(s) in the reference column corresponds to the reference item number in Appendix A from which the concentration range from previous studies was extracted.

[2] - The concentration ranges were derived from both combined bottom/fly and discrete bottom ash samples.

## TABLE 5.4 COMPARATIVE EVALUATION OF METALS IN EP LEACHATES

### FLY ASH

| Metal | Concentration Range From This Study (mg/L) | Concentration Range From Previous Studies (mg/L) | References [1] |
|---|---|---|---|
| Arsenic (As) | ND(0.01) | ND(0.001) - 0.858 | 30, 53 |
| Cadmium (Cd) | 6.02 - 18.0 | 0.025 - 100 | 42, 53 |
| Chromium (Cr) | ND(0.005) - 0.038 | 0.006 - 0.135 | 30, 53 |
| Copper (Cu) | 0.041 - 1.62 | 0.033 - 10.6 | 53 |
| Iron (Fe) | ND(0.005) - 0.49 | 0.189 - 0.202 | 53 |
| Lead (Pb) | 4.72 - 25.2 | 0.019 - 53.35 | 30, 53 |
| Manganese (Mn) | 2.71 - 8.03 | 0.005 - 5.79 | 53 |
| Mercury (Hg) | ND(0.008) | ND(0.0002) - 0.007 | 30, 53 |
| Nickel (Ni) | 0.137 - 1.92 | 0.09 - 2.90 | 53 |
| Selenium (Se) | ND(0.05) | ND(0.002) - 0.085 | 30, 53 |
| Zinc (Zn) | 186 - 726 | 3.36 - 768 | 53 |

### COMBINED ASH [2]

| Metal | Concentration Range From This Study (mg/L) | Concentration Range From Previous Studies (mg/L) | References [1] |
|---|---|---|---|
| Arsenic (As) | ND(0.01) | ND(0.001) - 0.122 | 30, 53 |
| Cadmium (Cd) | 0.06 - 0.827 | 0.018 - 3.94 | 30, 53 |
| Chromium (Cr) | 0.0059 - 0.150 | ND(0.007) - 0.46 | 30, 53 |
| Copper (Cu) | 0.039 - 1.19 | 0.713 - 0.898 | 53 |
| Iron (Fe) | 4.5 - 143 | 94.3 - 96.5 | 53 |
| Lead (Pb) | 2.09 - 34 | 0.02 - 21.0 | 53 |
| Manganese (Mn) | 3.60 - 6.24 | 5.62 - 6.21 | 53 |
| Mercury (Hg) | ND(0.008) | ND(0.0002) - 6.00 | 30, 53 |
| Nickel (Ni) | 0.241 - 0.415 | 0.463 - 2.03 | 53 |
| Selenium (Se) | ND(0.05) | ND(0.002) - 0.10 | 30, 53 |
| Zinc (Zn) | 38.5 - 726 | 64.5 - 81 | 53 |

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ND - Not Detected; the detection limit is given in parentheses following ND.

[1] - The number(s) in the reference column corresponds to the reference item number in Appendix A from which the concentration range from previous studies was extracted.

[2] - The concentration ranges were derived from both combined bottom/fly and discrete bottom ash samples.

## TABLE 5.5 COMPARATIVE EVALUATION OF METALS IN TCLP LEACHATES

### FLY ASH

| Metal | Concentration Range From This Study (mg/L) | Concentration Range From Previous Studies (mg/L) | References [1] |
|---|---|---|---|
| Arsenic (As) | ND(0.01) - 0.111 | N.A. | N/A |
| Cadmium (Cd) | 0.015 - 17.2 | 0.03 - 20.3 | 53 |
| Chromium (Cr) | ND(0.005) - 0.544 | 0.02 - 0.12 | 53 |
| Copper (Cu) | ND(0.005) - 0.201 | 0.02 - 14.7 | 53 |
| Iron (Fe) | ND(0.005) - 190 | 0.03 - 0.17 | 53 |
| Lead (Pb) | ND(0.05) - 15.2 | 5.3 - 36.6 | 53 |
| Manganese (Mn) | 0.049 - 14.7 | 0.01 - 7.19 | 53 |
| Mercury (Hg) | ND(0.008) | N.A. | N/A |
| Nickel (Ni) | ND(0.015) - 1.52 | 0.09 - 2.48 | 53 |
| Selenium (Se) | ND(0.005) | N.A. | N/A |
| Zinc (Zn) | 0.151 - 746 | 2.27 - 8.85 | 53 |

### COMBINED ASH [2]

| Metal | Concentration Range From This Study (mg/L) | Concentration Range From Previous Studies (mg/L) | References [1] |
|---|---|---|---|
| Arsenic (As) | ND(0.01) - 0.037 | 0.01 - 0.1 | 53 |
| Cadmium (Cd) | 0.025 - 3.32 | 0.01 - 1.9 | 53 |
| Chromium (Cr) | ND(0.005) - 0.439 | 0.01 - 0.32 | 53 |
| Copper (Cu) | ND(0.005) - 0.019 | 0.02 - 0.09 | 53 |
| Iron (Fe) | 0.828 - 60.6 | 2.18 - 230 | 53 |
| Lead (Pb) | 0.655 - 30.1 | 0.05 - 47 | 53 |
| Manganese (Mn) | 4.2 - 11.9 | 3.22 - 7.47 | 53 |
| Mercury (Hg) | ND(0.008) | ND(0.0002) - 0.10 | 53 |
| Nickel (Ni) | 0.346 - 0.805 | 0.09 - 0.41 | 53 |
| Selenium (Se) | ND(0.005) | 0.01 - 0.05 | 53 |
| Zinc (Zn) | 23.3 - 373 | 23.5 - 83.2 | 53 |

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N.A.- Not Available; N/A - Not Applicable

ND - Not Detected; the detection limit is given in parentheses following ND.

[1] - The number(s) in the reference column corresponds to the reference item number in Appendix A from which the concentration range from previous studies was extracted.

[2] - The concentration ranges were derived from both combined bottom/fly and discrete bottom ash samples.

nickel, and zinc. Again, these discrepancies may have been a result of the limited amount of data available in previous studies.

The concentration ranges for metals in deionized water leachates prepared from the fly ash and combined ash are presented in Table 5.6. Special care should be taken when comparing and evaluating the data in this table because the monofilled waste extraction procedure (MWEP; SW-924) was used by Versar, but the nature of the deionized water leaching procedure used in the previous study is not known. Nevertheless, Table 5.6 shows that the concentrations from this study for both the fly ash and combined ash are comparable to the concentrations from previous studies.

### 5.1.3 Field Water Samples

The concentration ranges for metals in field leachate and quench water samples are presented in Table 5.7. The field leachate results from this study are within the concentration ranges from the previous studies for every metal. Generally, the concentrations from this study are in the lower end of the concentration ranges from previous studies. Conversely, the quench water concentrations from this study exceed the upper boundary of the ranges from previous studies for metals. One possible explanation for this is that several of the quench water samples from this study contained appreciable amount of solids (i.e., ash material). Since total metals were quantified, the samples were subjected to the acid digestion and subsequent analysis without a filtration step. As a result, the quench water sample results may have been biased high in comparison to other studies by the solid materials. Nevertheless, the data reported in this study characterizes the quality of the wastewater which is discharged.

Table 5.8 presents the concentration ranges for organic constituents (BNAs) in field leachate and quench water samples. Both the field leachate and quench water results from this study are generally within the concentration ranges from the previous studies, where the data are

## TABLE 5.6 COMPARATIVE EVALUATION OF METALS IN DEIONIZED WATER LEACHATES

### FLY ASH

| Metal | Concentration Range From This Study (mg/L) | Concentration Range From Previous Studies (mg/L) | References [1] |
|---|---|---|---|
| Arsenic (As) | ND(0.01) | N.A. | N/A |
| Cadmium (Cd) | ND(0.01) - 0.122 | 0.03 - 0.17 | 53 |
| Chromium (Cr) | ND(0.005) - 0.15 | 0.04 - 0.08 | 53 |
| Copper (Cu) | ND(0.005) - 0.089 | ND(0.02) | 53 |
| Iron (Fe) | ND(0.005) - 0.167 | ND(0.03) | 53 |
| Lead (Pb) | ND(0.05) - 0.148 | 0.26 - 35.0 | 53 |
| Manganese (Mn) | ND(0.001) - 0.0052 | ND(0.01) | 53 |
| Mercury (Hg) | ND(0.02) | N.A. | N/A |
| Nickel (Ni) | ND(0.015) - 0.022 | ND(0.015) - 0.09 | 53 |
| Selenium (Se) | ND(0.005) - 0.108 | N.A. | N/A |
| Zinc (Zn) | ND(0.003) - 1.22 | 0.67 - 4.15 | 53 |

### COMBINED ASH [2]

| Metal | Concentration Range From This Study (mg/L) | Concentration Range From Previous Studies (mg/L) | References [1] |
|---|---|---|---|
| Arsenic (As) | ND(0.01) | ND(0.05) | 53 |
| Cadmium (Cd) | ND(0.01) | 0.01 - 0.03 | 53 |
| Chromium (Cr) | ND(0.005) | ND(0.01) - 0.02 | 53 |
| Copper (Cu) | ND(0.005) - 0.07 | 0.11 - 0.19 | 53 |
| Iron (Fe) | ND(0.005) - 0.038 | ND(0.03) | 53 |
| Lead (Pb) | ND(0.05) - 0.063 | ND(0.05) - 2.98 | 53 |
| Manganese (Mn) | ND(0.001) - 0.0021 | ND(0.01) | 53 |
| Mercury (Hg) | ND(0.02) | ND(0.10) | 53 |
| Nickel (Ni) | ND(0.015) | ND(0.02) - 0.09 | 53 |
| Selenium (Se) | ND(0.005) | ND(0.05) | 53 |
| Zinc (Zn) | ND(0.003) - 0.067 | 0.38 - 0.96 | 53 |

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N.A.- Not Available; N/A - Not Applicable

ND - Not Detected; the detection limit is given in parentheses following ND.

[1] - The number(s) in the reference column corresponds to the reference item number in Appendix A from which the concentration range from previous studies was extracted.

[2] - The concentration ranges were derived from both combined bottom/fly and discrete bottom ash samples.

TABLE 5.7 COMPARATIVE EVALUATION OF TOTAL METALS IN FIELD WATER SAMPLES

## FIELD LEACHATE

| Metal | Concentration Range From This Study (mg/L) | Concentration Range From Previous Studies (mg/L) | References [1] |
|---|---|---|---|
| Arsenic (As) | ND(0.01) - 0.218 | ND(0.05) - 70.2 | 30, 52 |
| Cadmium (Cd) | ND(0.005) - 0.044 | ND(0.01) - 17.0 | 30, 52 |
| Chromium (Cr) | ND(0.005) - 0.914 | ND(0.006) - 33.4 | 30, 52, 69 |
| Copper (Cu) | 0.045 - 2.57 | ND(0.006) - 24.0 | 30, 52 |
| Iron (Fe) | 0.758 - 121 | ND(0.007) - 5,500 | 30, 52, 69 |
| Lead (Pb) | ND(0.05) - 2.92 | ND(0.001) - 14.2 | 52 |
| Manganese (Mn) | 0.103 - 4.57 | ND(0.002) - 1,400 | 52 |
| Mercury (Hg) | ND(0.0002) - 0.008 | ND(0.002) - 0.064 | 30, 52 |
| Nickel (Ni) | ND(0.015) - 0.412 | ND(0.05) - 7.5 | 30, 52 |
| Selenium (Se) | ND(0.005) - 0.037 | ND(0.01) | 30 |
| Zinc (Zn) | 0.048 - 3.30 | ND(0.01) - 1,000 | 30, 52 |

## QUENCH WATER

| Metal | Concentration Range From This Study (mg/L) | Concentration Range From Previous Studies (mg/L) | References [1] |
|---|---|---|---|
| Arsenic (As) | ND(0.01) - 0.542 | ND(0.001) - 0.0031 | 46, 56 |
| Cadmium (Cd) | ND(0.005) - 1.91 | ND(0.004) - 0.067 | 46, 56 |
| Chromium (Cr) | 0.0085 - 1.12 | ND(0.007) - 0.014 | 46, 56 |
| Copper (Cu) | 0.02 - 13.1 | ND(0.006) | 46 |
| Iron (Fe) | 0.037 - 141 | ND(0.007) | 46 |
| Lead (Pb) | 0.176 - 37.9 | ND(0.001) - 0.688 | 46, 56 |
| Manganese (Mn) | 0.024 - 12.6 | ND(0.002) | 46 |
| Mercury (Hg) | ND(0.0002) - 0.022 | ND(0.0002) - 0.0089 | 46, 56 |
| Nickel (Ni) | 0.009 - 0.849 | ND(0.015) | 46 |
| Selenium (Se) | ND(0.0125) | ND(0.002) - 0.036 | 46, 56 |
| Zinc (Zn) | 0.087 - 192 | ND(0.002) | 46 |

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ND - Not Detected; the detection limit is given in parentheses following ND.

[1] - The number(s) in the reference column corresponds to the reference item number in Appendix A from which the concentration range from previous studies was extracted.

## TABLE 5.8 COMPARATIVE EVALUATION OF BNAs IN FIELD WATER SAMPLES

### FIELD LEACHATE

| BNA Compound | Concentration Range From This Study (ug/L) | Concentration Range From Previous Studies (ug/L) | References [1] |
|---|---|---|---|
| Biphenyl | ND(N.A.) - 51 | N.A. | N/A |
| Di-n-butyl phthalate | ND(2.5) | ND(2.5) - 150 | 52 |
| Diethyl phthalate | ND(22) | ND(2.2) - 300 | 52 |
| Dimethyl phthalate | ND(1.6) | ND(1.6) - 55 | 52 |
| Dimethyl propanediol | ND(N.A.) - 120 | N.A. | N/A |
| Bis 2-ethylhexyl phthalate | ND(2.5) - 80 | ND(2.5) - 150 | 52 |
| Naphthalene | ND(1.6) | ND(1.6) - 19 | 52 |
| Phenol | ND(1.5) | ND(1.5) - 29,800 | 52 |
| Thiolane | ND(N.A.) - 400 | N.A. | N/A |

### QUENCH WATER

| BNA Compound | Concentration Range From This Study (ug/L) | Concentration Range From Previous Studies (ug/L) | References [1] |
|---|---|---|---|
| Acenaphthylene | ND(3.5) - 6.0 | 0.46 - 28 | 35 |
| Benzoic acid | ND(N.A.) - 3,800 | N.A. | N/A |
| Di-n-butyl phthalate | ND(2.5) - 3.0 | ND(0.6) - 13 | 35 |
| Bis 2-ethylhexyl phthalate | ND(2.5) - 8.0 | ND(0.6) - 1.8 | 35 |
| Fluoranthene | ND(2.2) - 6.0 | 0.45 - 1.5 | 35 |
| Hexanoic acid | ND(N.A.) - 920 | N.A. | N/A |
| 2-Hydroxybenzoic acid | ND(N.A.) - 50 | N.A. | N/A |
| Methylpentanoic acid | ND(N.A.) - 88 | N.A. | N/A |
| 2-Methyl phenol | ND(2.7) - 86 | N.A. | N/A |
| 4-Methyl phenol | ND(2.7) - 94 | N.A. | N/A |
| Naphthalene | ND(1.6) - 8.0 | ND(0.6) - 3.0 | 35 |
| Phenanthrene | ND(5.4) - 6.0 | ND(0.6) - 5.0 | 35 |
| Phenol | ND(1.5) - 640 | N.A. | N/A |
| Pyrene | ND(1.9) - 5.0 | 0.57 - 4.4 | 35 |

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N.A.- Not Available; N/A - Not Applicable

ND - Not Detected; the detection limit is given in parentheses following ND.

[1] - The number(s) in the reference column corresponds to the reference item number in Appendix A from which the concentration range from previous studies was extracted.

available. The results of both this study and the previous studies indicate that the polycyclic aromatic hydrocarbons (e.g., acenaphthylene, fluoranthene, naphthalene, phenanthrene, and pyrene), the phthalate esters (e.g., bis-2-ethylhexyl phthalate, di-n-butyl phthalate, diethyl phthalate, and dimethyl phthalate), and the phenols (e.g., phenol, methyl phenol, and dimethyl phenol) are the predominant BNA compounds that were detected in the field water samples.

## 5.2 Significant Trends in the Data from this Study

The data generated from the samples collected in this study were summarized by facility and sample type (e.g., ground water, field leachate, fly ash, combined ash EP leachate, etc.) to facilitate data evaluation. The data summaries were generated by averaging the individual analytical results for each sample type from each facility. One summary was prepared for the metals data, and another one was prepared for the PCBs, PCDDs, and PCDFs. A summary was not prepared for the BNAs because very few of the individual BNA constituents were detected often enough to allow for a meaningful comparative evaluation.

### 5.2.1 Metals

The summary of the metals data is presented in Table 5.9. The metals data for the solid samples showed that the fly ash contained more total metals than the combined (i.e., bottom/fly) ash or the bottom ash. The fly ash consistently exhibited higher concentrations of cadmium, chromium, lead, nickel, zinc, arsenic, mercury, and selenium than the combined ash or bottom ash. However, the combined ash and bottom ash contained higher concentrations of copper and iron. The fly ash contained approximately the same amount of manganese as the combined ash and bottom ash. These observations suggest that the which tend to become more concentrated in the fly ash are the more volatile metals, while those metals that are more highly concentrated in the combined ash and bottom are the higher boiling point less volatile metals.

## TABLE 5.9 SUMMARY RESULTS FOR METALS

### FACILITY A

| Sample Type | Sample Matrix | Units | Cd | Cr | Cu | Fe | Pb | Mn | Ni | Zn | As | Hg | Se |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Fly Ash | Solid | mg/kg | 190.8 | 70.8 | 1716 | 15646 | 5636 | 997 | 110 | 14436 | 36.3 | 26.8 | 2.5 |
| Fly Ash | EP Tox. | mg/L | 6.87 | <0.005 | 0.15 | <0.005 | 7.76 | 7.32 | 0.396 | 224 | <0.01 | <0.008 | <0.05 |
| Fly Ash | TCLP | mg/L | 0.023 | 0.136 | <0.005 | 190 | 0.962 | 2.33 | 0.372 | 38.9 | 0.024 | <0.008 | <0.025 |
| Fly Ash | SW924-EX1 | mg/L | <0.015 | 0.01 | 0.058 | 0.167 | <0.075 | 0.004 | 0.0225 | 0.036 | <0.01 | <0.04 | <0.05 |
| Fly Ash | SW924-EX2 | mg/L | <0.01 | <0.005 | 0.009 | 0.057 | 0.072 | 0.003 | <0.015 | 0.083 | <0.01 | <0.02 | <0.005 |
| Bottom/Fly | Solid | mg/kg | 19.8 | 16.8 | 356 | 5904 | 1246 | 247 | 22.0 | 2010 | 6.8 | 6.3 | 1.4 |
| Bottom/Fly | EP Tox. | mg/L | 0.827 | 0.016 | 1.19 | 4.50 | 20.8 | 4.15 | 0.241 | 38.5 | <0.01 | <0.008 | <0.05 |
| Bottom/Fly | TCLP | mg/L | 0.682 | 0.096 | 0.019 | 60.6 | 16.3 | 7.18 | 0.346 | 55.8 | 0.020 | <0.008 | <0.05 |
| Bottom/Fly | SW924-EX1 | mg/L | <0.01 | <0.005 | <0.005 | <0.005 | <0.05 | <0.001 | <0.015 | <0.003 | <0.01 | <0.02 | <0.005 |
| Bottom/Fly | SW924-EX2 | mg/L | <0.01 | <0.005 | <0.005 | <0.005 | <0.005 | <0.001 | <0.015 | 0.0031 | <0.01 | <0.02 | <0.005 |
| Quench | Water | mg/L | 0.09 | 0.016 | 0.185 | 1.48 | 5.005 | 0.1355 | 0.009 | 5.475 | 0.011 | 0.0117 | 0.005 |
| Groundwater | Water | mg/L | <0.005 | 0.0067 | 0.0086 | 2.89 | <0.050 | 0.107 | <0.018 | 0.029 | <0.010 | <0.0002 | <0.005 |

### FACILITY B

| Sample Type | Sample Matrix | Units | Cd | Cr | Cu | Fe | Pb | Mn | Ni | Zn | As | Hg | Se |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Fly Ash | Solid | mg/kg | 349 | 94.8 | 765 | 12742 | 8706 | 998 | 69 | 32180 | 111.0 | 13.9 | 9.5 |
| Fly Ash | EP Tox. | mg/L | 18 | <0.005 | 0.171 | 0.060 | 19.3 | 4.65 | 0.137 | 726 | <0.01 | <0.008 | <0.05 |
| Fly Ash | TCLP | mg/L | 17.2 | <0.005 | 0.078 | 0.019 | 6.91 | 3.97 | 0.076 | 275 | <0.01 | <0.008 | <0.05 |
| Fly Ash | SW924-EX1 | mg/L | <0.01 | 0.0086 | <0.005 | <0.005 | <0.05 | 0.0024 | <0.015 | 0.026 | <0.01 | <0.02 | <0.05 |
| Fly Ash | SW924-EX2 | mg/L | 0.033 | 0.01 | 0.012 | 0.118 | 0.148 | 0.0052 | <0.015 | 1.2 | <0.01 | <0.02 | <0.025 |
| Bottom Ash | Solid | mg/kg | 10.74 | 61.2 | 4209 | 39140 | 2800 | 887 | 41.4 | 4671 | 9.20 | 0.17 | 2.50 |
| Bottom Ash | EP Tox. | mg/L | 0.388 | 0.15 | 0.127 | 21.0 | 34.0 | 3.60 | 0.250 | 58.4 | <0.01 | <0.008 | <0.05 |
| Bottom Ash | TCLP | mg/L | 0.418 | 0.439 | 0.018 | 52.8 | 30.1 | 6.82 | 0.473 | 83.2 | 0.037 | <0.008 | <0.05 |
| Bottom Ash | SW924-EX1 | mg/L | <0.01 | <0.005 | 0.0089 | <0.005 | <0.05 | <0.001 | <0.015 | <0.003 | <0.01 | <0.02 | <0.025 |
| Bottom Ash | SW924-EX2 | mg/L | <0.01 | <0.005 | <0.005 | 0.024 | <0.05 | 0.0012 | <0.015 | 0.018 | <0.01 | <0.02 | <0.005 |
| Field Leachate | Water | mg/L | 0.018 | 0.0097 | 0.0973 | 13.0593 | 0.0853 | 1.7103 | 0.0205 | 0.0817 | 0.0050 | 0.0009 | 0.0058 |
| Quench | Water | mg/L | 0.0025 | 0.019 | 0.0363 | 0.2647 | 0.2380 | 0.0617 | 0.0090 | 0.1693 | 0.0050 | 0.0007 | 0.0050 |
| Groundwater | Water | mg/L | 0.0081 | 0.0054 | 0.012 | 0.971 | <0.050 | 1.57 | <0.018 | 0.039 | <0.010 | <0.0002 | <0.025 |

# TABLE 5.9 SUMMARY RESULTS FOR METALS

## FACILITY C

| Sample Type | Sample Matrix | Units | Cd | Cr | Cu | Fe | Pb | Mn | Ni | Zn | As | Hg | Se |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Fly Ash | Solid | mg/kg | 173.2 | 55.8 | 621 | 11356 | 3226 | 357 | 157 | 9900 | 24.4 | 3.0 | 7.0 |
| Fly Ash | EP Tox. | mg/L | 7.89 | 0.038 | 1.62 | 0.490 | 17.8 | 2.71 | 1.92 | 362 | <0.01 | <0.008 | <0.05 |
| Fly Ash | TCLP | mg/L | 8.36 | 0.129 | 0.201 | 34.2 | 13.4 | 5.14 | 1.52 | 446 | 0.036 | <0.008 | <0.025 |
| Fly Ash | SW924-EX1 | mg/L | 0.122 | 0.006 | 0.045 | 0.067 | 0.128 | 0.014 | <0.015 | 1.22 | <0.01 | <0.02 | 0.108 |
| Fly Ash | SW924-EX2 | mg/L | <0.01 | <0.005 | <0.005 | <0.005 | <0.05 | <0.001 | <0.015 | <0.003 | <0.01 | <0.02 | <0.025 |
| Bottom/Fly | Solid | mg/kg | 17.8 | 87.2 | 3231 | 11656 | 4634 | 534 | 154.6 | 1973 | 8.8 | 0.4 | 1.8 |
| Bottom/Fly | EP Tox. | mg/L | 0.06 | 0.0059 | 0.039 | 143 | 2.09 | 4.11 | 0.337 | 726 | <0.01 | <0.008 | <0.05 |
| Bottom/Fly | TCLP | mg/L | 3.32 | <0.005 | 0.0076 | 23.4 | 7.30 | 11.9 | 0.805 | 373 | <0.01 | <0.008 | <0.05 |
| Bottom/Fly | SW924-EX1 | mg/L | <0.01 | <0.005 | 0.023 | 0.038 | 0.063 | 0.0021 | <0.015 | 0.067 | <0.01 | <0.02 | <0.05 |
| Bottom/Fly | SW924-EX2 | mg/L | <0.01 | <0.005 | <0.005 | 0.015 | <0.05 | <0.001 | <0.015 | 0.051 | <0.01 | <0.02 | <0.005 |
| Perimeter Comp. | Solid | mg/kg | 8.7 | 85 | 1190 | 60600 | 709 | 572 | 120 | 4740 | 6.0 | 0.57 | <5 |
| Field Leachate | Water | mg/L | 0.0117 | 0.3101 | 0.9383 | 44.9107 | 1.0043 | 0.8257 | 0.1488 | 0.6927 | 0.0827 | 0.0028 | 0.0207 |
| Quench | Water | mg/L | 0.128 | 0.0119 | 0.065 | 1.4005 | 0.2510 | 0.7200 | 0.1085 | 8.3550 | 0.0050 | 0.0003 | 0.0050 |
| Groundwater | Water | mg/L | <0.010 | <0.005 | 0.015 | 1.52 | <0.050 | 0.051 | <0.015 | 0.0056 | 0.013 | <0.0002 | <0.025 |

## FACILITY D

| Sample Type | Sample Matrix | Units | Cd | Cr | Cu | Fe | Pb | Mn | Ni | Zn | As | Hg | Se |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Fly Ash | Solid | mg/kg | 226.6 | 83.2 | 525 | 8486 | 4998 | 1092 | 76 | 19900 | 51.2 | 1.4 | 10.9 |
| Fly Ash | EP Tox. | mg/L | 8.89 | <0.005 | 0.086 | 0.01 | 22.4 | 7.17 | 0.286 | 444 | <0.01 | <0.008 | <0.05 |
| Fly Ash | TCLP | mg/L | 9.6 | 0.516 | 0.012 | 13.9 | 14 | 14.2 | 0.575 | 685 | 0.099 | <0.008 | <0.05 |
| Fly Ash | SW924-EX1 | mg/L | 0.015 | 0.093 | 0.005 | <0.005 | <0.05 | 0.0061 | <0.015 | 0.108 | <0.01 | <0.02 | 0.047 |
| Fly Ash | SW924-EX2 | mg/L | <0.01 | 0.133 | <0.005 | <0.005 | <0.05 | 0.002 | <0.015 | 0.019 | <0.01 | <0.02 | <0.025 |
| Bottom/Fly | Solid | mg/kg | 24.2 | 35.2 | 605 | 31038 | 1220 | 1115 | 57.8 | 11132 | 7.7 | 0.1 | 0.8 |
| Bottom/Fly | EP Tox. | mg/L | 0.649 | 0.033 | 0.051 | 66.4 | 7.26 | 6.24 | 0.415 | 61.7 | <0.01 | <0.008 | <0.05 |
| Bottom/Fly | TCLP | mg/L | 0.025 | <0.005 | <0.005 | 0.828 | 0.655 | 4.20 | 0.573 | 23.3 | <0.01 | <0.008 | <0.005 |
| Bottom/Fly | SW924-EX1 | mg/L | <0.01 | 0.005 | 0.07 | <0.005 | <0.05 | <0.001 | <0.015 | <0.003 | <0.01 | <0.02 | <0.005 |
| Bottom/Fly | SW924-EX2 | mg/L | <0.01 | <0.005 | 0.009 | 0.01 | <0.05 | <0.001 | <0.015 | 0.0034 | <0.01 | <0.02 | <0.005 |
| Perimeter Comp. | Solid | mg/kg | 30 | 52 | 402 | 19600 | 1210 | 455 | 51 | 2050 | 14.8 | 0.25 | <2.5 |
| Field Leachate | Water | mg/L | 0.0188 | 0.0993 | 0.529 | 34.8767 | 0.8230 | 0.3380 | 0.1407 | 2.2047 | 0.0210 | 0.0005 | 0.0092 |
| Quench | Water | mg/L | 1.335 | 0.725 | 6.49 | 77.4000 | 28.2667 | 10.2233 | 0.4537 | 129.53 | 0.3370 | 0.0153 | 0.0050 |

The analytical results for the metals in the landfill perimeter composite were expected to approximate the results for the combined ash samples from the corresponding facilities. Although some slight variations were noted, the data in Table 5.9 showed that the metals concentrations for the perimeter composite and combined ash samples were approximately equal. The slight variations can be attributed to the effects of weathering on the older ash, the heterogeneity of the ash materials, and the variability of the raw refuse that is incinerated at the facility. These observations suggest that the amount of leachable metals present in the disposed ash is a relatively small percentage of the total metals.

The quench water at all four facilities is discharged to the local publicly owned treatment works (POTW). In general, the analyses of the quench water samples indicated that the quality of the quench water was suitable for discharge to a POTW. However, the quench water from Facility D had extremely high concentrations of metals because the samples were collected from the quench water tank and contained an appreciable quantity of solid materials.

Field leachate samples were collected from natural seeps at three facilities of the four facilities tested. The leachate discharges are not controlled or treated at any of the facilities. Therefore, they eventually percolate into the ground or flow into nearby surface waters. The field leachate data in Table 5.9 showed that the metals concentrations at all three facilities were essentially equal, despite the fact that the solid samples of the ash materials disposed at the three landfills contained significantly different metals concentrations. This suggests that the leachable metal components in the ash do not vary in direct proportion with the total metals concentration.

A comparison of the metals concentrations in the quench water and field leachate showed that the field leachates generally contain slightly higher concentrations of metals. This suggests that the metals leach slowly from the landfills at a relatively constant rate, and that they usually are not leached in the quench water tank.

The laboratory-prepared leachate metals data in Table 5.9 indicated that the EP and TCLP methods are more aggressive for extracting metals than the SW-924 procedure. This was expected because an acidic leaching solution is used for both the EP and TCLP methods, while in the SW-924 procedure, a neutral leaching solution (i.e., deionized water) is used. The EP and TCLP procedures appeared to have approximately equal extraction efficiencies for cadmium, copper, iron, nickel, zinc, mercury, and selenium. The EP method appeared to extract lead slightly more efficiently than the TCLP method, but the TCLP method appeared to be slightly more efficient for extracting arsenic, chromium, and manganese.

Upon comparing the laboratory leachate metals data for the fly ash with the combined ash and bottom ash, the following trends were noted. Although the fly ash solids contained higher concentrations of cadmium, chromium, lead, nickel, and zinc than the combined ash and bottom ash solids, the fly ash leachates contained higher concentrations than the combined ash and bottom ash leachates for cadmium. This suggests that the leachable fractions of chromium, lead, nickel, and zinc are inherent in the bottom ash. Similarly, the combined ash and bottom ash solids exhibited higher concentrations of copper and iron than the fly ash solids. However, the combined ash and bottom ash leachates contained higher concentrations than the fly ash leachates for iron. This indicates that the component of the total copper is inherent in the fly ash. Finally, the total manganese concentrations were approximately equal for the fly ash solids and the bottom ash and combined ash solids; however, the combined ash and bottom ash leachate contained slightly higher manganese concentrations than the fly ash leachates. Therefore, the leachable fraction of manganese appears to be inherent in the bottom ash.

A comparison of the metals concentrations in the field leachates with those in the laboratory-prepared leachates showed that the EP and

TCLP methods approximated the natural leaching conditions for chromium, copper, iron, nickel, arsenic, mercury, and selenium better than the SW-924 procedure. Conversely, the SW-924 procedure appeared to better correlate with the natural leaching conditions for cadmium, lead, manganese, and zinc.

For the ground-water metals data, the concentrations were generally negligible for all metals except iron. Therefore, it does not appear that the natural field leachate is having a deleterious effect on the ground water. However, no ground-water data were available to describe background (i.e., upgradient from the landfill) conditions. At each facility, with the possible exception of Facility C, the quality of the monitoring wells systems including the design and locations of the monitoring wells may not have been adequate to detect releases from the landfill areas. Therefore, the actual magnitude of the natural leachate's effect on the ground water could not be discerned.

### 5.2.2 Polychlorinated Biphenyls, Polychlorinated Dibenzo-p-dioxins, and Polychlorinated Dibenzo-furans

The analytical results for the PCBs, PCDDs, and PCDFs are summarized by facility in Table 5.10. The PCB, PCDD, and PCDF results for the solid samples showed that the fly ash consistently contained higher concentrations of PCBs, PCDDs, and PCDFs than the combined ash and bottom ash. The data also showed that the PCDDs were generally more concentrated than the PCDFs and the PCBs in all sample types. Similarly, the PCDFs were much more concentrated than the PCBs for all sample types.

The field water sample results indicated that negligible quantities of PCBs were present in these matrices, and only minor quantities of PCDDs and PCDFs were identified. This suggests that the PCBs, PCDDs, and PCDFs are not mobile in the natural environment through aqueous transport pathways. The PCDD and PCDF results for the TCLP- prepared laboratory leachates were not presented in Table 5.10 because they were generally near, or below, the detection limit. This suggests that the TCLP does not extract PCDD and PCDF constituents effectively.

## TABLE 5.10 SUMMARY RESULTS FOR PCBs, DIOXINS AND FURANS

| Plant | Sample Type | Sample Matrix | Units | MONO -CB | DI -CB | TRI -CB | TETRA -CB | PENTA -CB | TOTAL PCB |
|---|---|---|---|---|---|---|---|---|---|
| A | Fly Ash | Solid | ng/g | 0.64 | 0.73 | 0.52 | | | 0.82 |
| A | Bottom/Fly | Solid | ng/g | | 0.66 | | | | 0.66 |
| A | Quench | Water | ug/L | | 0.004 | | | | 0.004 |

| Plant | Sample Type | Sample Matrix | Units | Species | 2,3,7,8 | TETRA | PENTA | HEXA | HEPTA | OCTA | TOTAL | TCDD + TCDF |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A | Fly Ash | Solid | ng/g | Dioxin | 0.16 | 4.32 | 18.60 | 23.40 | 16.40 | 18.00 | 80.7 | |
| A | Fly Ash | Solid | ng/g | Furan | | 43.6 | 16.0 | 33.6 | 20.4 | 2.4 | 116.0 | 196.7 |
| A | Bottom/Fly | Solid | ng/g | Dioxin | 0.14 | 5.57 | 8.30 | 4.97 | 3.80 | 1.81 | 24.44 | |
| A | Bottom/Fly | Solid | ng/g | Furan | 5.09 | 39.10 | 15.40 | 7.50 | 2.81 | 0.59 | 65.4 | 89.8 |
| A | Quench | Water | ng/l | Dioxin | <0.08 | 2 | 4 | 2 | 1.9 | 0.98 | 10.88 | |
| A | Quench | Water | ng/l | Furan | 2.1 | 12 | 6.1 | 3.1 | 1.2 | 0.27 | 24.77 | 35.65 |

| Plant | Sample Type | Sample Matrix | Units | MONO -CB | DI -CB | TRI -CB | TETRA -CB | PENTA -CB | TOTAL PCB |
|---|---|---|---|---|---|---|---|---|---|
| B | Fly Ash | Solid | ng/g | 0.40 | 1.19 | 2.20 | 2.56 | 0.87 | 3.66 |
| B | Bottom Ash | Solid | ng/g | | | | | | 0 |
| B | Quench | Water | ug/L | 0.03 | | | | | 0.03 |
| B | Field Leachate | Water | ug/L | | | | | | 0 |

| Plant | Sample Type | Sample Matrix | Units | Species | 2,3,7,8 | TETRA | PENTA | HEXA | HEPTA | OCTA | TOTAL | TCDD + TCDF |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| B | Fly Ash | Solid | ng/g | Dioxin | 0.35 | 10.90 | 114.60 | 197 | 237 | 469 | 1028 | |
| B | Fly Ash | Solid | ng/g | Furan | | 80.4 | 54.6 | 90.6 | 42.2 | 16.5 | 284 | 1313 |
| B | Bottom Ash | Solid | ng/g | Dioxin | 0.03 | 0.17 | 0.45 | 0.52 | 1.38 | 6.06 | 8.54 | |
| B | Bottom Ash | Solid | ng/g | Furan | 0.10 | 0.49 | 0.42 | 0.59 | 1.47 | 0.78 | 3.74 | 12.29 |
| B | Quench | Water | ng/l | Dioxin | <0.07 | <0.07 | <0.05 | <0.04 | 0.05 | 0.13 | 0.18 | |
| B | Quench | Water | ng/l | Furan | <0.08 | <0.08 | <0.04 | <0.02 | 0.04 | <0.30 | 0.04 | 0.22 |
| B | Field Leachate | Water | ng/l | Dioxin | 0.28 | 6.6 | 25 | 22 | 21 | 14 | 88.6 | |
| B | Field Leachate | Water | ng/l | Furan | 3.7 | 22 | 17 | 16 | 9.4 | 1.9 | 66.3 | 154.9 |

## TABLE 5.10 SUMMARY RESULTS FOR PCBs, DIOXINS AND FURANS

| Plant | Sample Type | Sample Matrix | Units | MONO -CB | DI -CB | TRI -CB | TETRA -CB | PENTA -CB | TOTAL PCB |
|---|---|---|---|---|---|---|---|---|---|
| C | Fly Ash | Solid | ng/g |  | 0.65 |  |  |  | 0.65 |
| C | Bottom/Fly | Solid | ng/g |  |  |  |  |  | 0 |
| C | Perimeter Comp. | Solid | ng/g |  | 41.5 | 225 | 109 |  | 375.5 |
| C | Quench | Water | ug/L | 0.02 |  |  |  |  | 0.02 |
| C | Field Leachate | Water | ug/L |  | 0.002 |  |  |  | 0.002 |
| C | Groundwater | Water | ug/L |  |  |  |  |  | 0 |

| Plant | Sample Type | Sample Matrix | Units | Species | 2,3,7,8 | TETRA | PENTA | HEXA | HEPTA | OCTA | TOTAL | TCDD + TCDF |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C | Fly Ash | Solid | ng/g | Dioxin | 1.95 | 27.2 | 500 | 2299 | 1837 | 1782 | 6445 |  |
| C | Fly Ash | Solid | ng/g | Furan | 13.3 | 102 | 152 | 635 | 281 | 128 | 1297 | 7742 |
| C | Bottom/Fly | Solid | ng/g | Dioxin | 0.36 | 6.50 | 25.8 | 37.4 | 61.6 | 44.3 | 176 |  |
| C | Bottom/Fly | Solid | ng/g | Furan | 1.79 | 11.42 | 12.50 | 16.54 | 16.80 | 4.08 | 61.34 | 237 |
| C | Perimeter Comp. | Solid | ng/g | Dioxin | 0.07 | 1.2 | 5.7 | 6.8 | 9 | 6.1 | 28.8 |  |
| C | Perimeter Comp. | Solid | ng/g | Furan | 0.51 | 2.4 | 3.9 | 4 | 3.3 | 0.81 | 14.41 | 43.21 |
| C | Quench | Water | ng/l | Dioxin | <0.81 | 0.59 | 5.9 | 10 | 19 | 12 | 47.49 |  |
| C | Quench | Water | ng/l | Furan | 0.55 | 2.4 | 4 | 6.2 | 6.5 | 1.4 | 20.5 | 67.99 |
| C | Field Leachate | Water | ng/l | Dioxin | 1.6 | 28 | 93 | 130 | 172 | 120 | 543 |  |
| C | Field Leachate | Water | ng/l | Furan | 11 | 65 | 64 | 76 | 60 | 15 | 280 | 823 |

| Plant | Sample Type | Sample Matrix | Units | MONO -CB | DI -CB | TRI -CB | TETRA -CB | PENTA -CB | TOTAL PCB |
|---|---|---|---|---|---|---|---|---|---|
| D | Fly Ash | Solid | ng/g | 0.94 | 4.00 | 3.91 | 2.48 | 2.25 | 11.41 |
| D | Bottom/Fly | Solid | ng/g |  | 0.71 | 6.52 | 16.50 |  | 3.42 |
| D | Perimeter Comp. | Solid | ng/g |  | 0.689 | 2.36 | 1.54 |  | 4.589 |
| D | Quench | Water | ug/L |  |  |  |  |  | 0 |
| D | Field Leachate | Water | ug/L |  |  | 0.008 |  |  | 0.008 |

| Plant | Sample Type | Sample Matrix | Units | Species | 2,3,7,8 | TETRA | PENTA | HEXA | HEPTA | OCTA | TOTAL | TCDD + TCDF |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| D | Fly Ash | Solid | ng/g | Dioxin | 0.54 | 9.64 | 59.4 | 90.4 | 50.0 | 55.4 | 265 |  |
| D | Fly Ash | Solid | ng/g | Furan |  | 57.6 | 33 | 69.4 | 47.6 | 5.4 | 213 | 478 |
| D | Bottom/Fly | Solid | ng/g | Dioxin | 0.07 | 0.75 | 2.70 | 2.03 | 1.95 | 1.63 | 9.02 |  |
| D | Bottom/Fly | Solid | ng/g | Furan | 0.56 | 3.48 | 2.63 | 2.10 | 1.34 | 0.33 | 9.86 | 18.88 |
| D | Perimeter Comp. | Solid | ng/g | Dioxin | 0.15 | 2.5 | 6 | 4.1 | 4.2 | 3.9 | 20.7 |  |
| D | Perimeter Comp. | Solid | ng/g | Furan | 1.3 | 11 | 7.7 | 5.3 | 2.7 | 0.61 | 27.31 | 48.01 |
| D | Quench | Water | ng/l | Dioxin | 17 | 700 | 650 | 450 | 420 | 330 | 2550 |  |
| D | Quench | Water | ng/l | Furan | 99 | 590 | 460 | 390 | 280 | 68 | 1788 | 4338 |
| D | Field Leachate | Water | ng/l | Dioxin | <0.26 | 0.27 | <0.22 | 2.1 | 8.8 | 25 | 36.17 |  |
| D | Field Leachate | Water | ng/l | Furan | 0.4 | 2.9 | 2.4 | 1.9 | 1.2 | 0.81 | 9.21 | 45.38 |

Two observations were noted from a comparison of the PCB, PCDD, and PCDF results for all of the sample types. First, there appeared to be an inverse relationship between the PCB and PCDD/PCDF concentrations (i.e., as the concentration for one of the constituents increased, the concentration for the other constituent decreased). Second, the PCDDs and PCDFs appeared to be directly proportional (i.e., as the concentration for one of the constituents increased, the concentration for the other constituent increased), although there did not appear to be any relationship between the relative abundance of either PCDDs or PCDFs in the total PCDD/PCDF concentration. These observations suggest that the favorable conditions for PCDD and PCDF formation are similar, while the favorable conditions for formation of PCBs are unfavorable for the formation of PCDDs and PCDFs.

## 5.3 Relationships Between Facility Design and Operating Characteristics and Contaminant Concentrations

In this section, the trends observed in Section 5.2 were evaluated with the facility design and operating characteristics in an attempt to explain the trends. Section 5.3.1 presents the evaluation for the metals data, and Section 5.3.2 presents the evaluation for the PCB, PCDD, and PCDF data.

### 5.3.1 Metals

There did not appear to be any significant correlation between the operating characteristics of the facilities and the metals concentrations in the residue. In general, the concentration of metal in the residues is a function of the raw refuse (i.e., incinerator feed material) composition. Although the distribution of metals between the fly ash and bottom ash did not appear to be a function of the facility operating characteristics, it did appear to be influenced by design features of the incinerator. For example, a rotary kiln incinerator with refuse processing (e.g., crushing or shredding) would be expected to have a significantly higher concentration of metals in the fly ash than a reciprocating grate incinerator without refuse processing. This is expected because crushing or shredding reduce the particle size, and the action of the rotary kiln results in autogenous grinding (i.e., the attrition and impaction between the particles), which also causes reduced particle size.

### 5.3.2 Polychlorinated Biphenyls, Polychlorinated Dibenzo-p-dioxins, and Polychlorinated Dibenzo-furans

Comparisons between operating characteristics/facility design and PCB, PCDD, and PCDF concentrations in the residues revealed the following observations. First, the PCB concentrations in both the fly ash and bottom ash increased with decreasing incineration temperatures. Second, the PCB concentrations were higher for the water-wall grate incinerators (Facilities B and D) than for the other facility types. Third, both the total PCDDs and the individual PCDD homologs increased in the fly ash as the incinerator temperature increased. Fourth, no correlations were observed between the facility design and operating characteristics and the bottom ash concentrations of PCDDs or PCDFs. Finally, the PCDD and PCDF concentrations for both the fly ash and the bottom ash were the highest for the combination rotary kiln/reciprocating grate facility (Facility C), and these concentrations were the lowest for the water-wall grate facilities (Facilities B and D), where the concentrations between facilities were approximately equal.

## 5.4 Overall Assessment of Risk

The risks associated with current MWC facility practices were assessed based on comparisons with applicable standards and criteria. Section 5.4.1 provides the comparisons for the metals data. Section 5.4.2 presents an evaluation of the risks associated with the PCBs found in MWC residues. Finally, Section 5.4.3 presents the risk assessment for the PCDDs found in MWC residues.

### 5.4.1 Metals

The results of the fly ash and combined bottom/fly ash and bottom ash samples prepared by the EP and TCLP procedures were compared to the RCRA Maximum Allowable Concentrations for arsenic, cadmium, chromium, lead, mercury, and selenium. The RCRA criteria for these six metals are as follows: arsenic = 5.0 mg/L; cadmium = 1.0 mg/L; chromium = 5.0 mg/L; lead = 5.0 mg/L; mercury = 0.2 mg/L; and selenium = 1.0 mg/L. Six fly ash samples were extracted using the EP method, and these leachates were analyzed for metals. The results of these analyses (see Table 4.8) indicated that none of the samples were above the RCRA criteria for arsenic, chromium, mercury, or selenium. However, 100 percent (6 out of 6) of the EP fly ash leachates exceeded the RCRA criterion for cadmium. The maximum cadmium concentration in an EP fly ash leachate was 18.0 mg/L. Similarly, 83 percent (5 out of 6) of the fly ash leachates failed the RCRA criterion for lead. The maximum lead concentration was 25.2 mg/L.

Three combined ash and one bottom ash samples were prepared using the EP method and analyzed. The results of these leachate analyses (see Table 4.8) showed that all of the EP leachates were below the RCRA criteria for arsenic, cadmium, chromium, mercury, and selenium. However, 75 percent (3 out of 4) combined and bottom ash leachates exceeded the RCRA criterion for lead. The maximum lead concentration was 34.0 mg/L.

The results for the TCLP-prepared leachates were similar. For the fly ash, 67 percent (4 out of 6) of the TCLP leachates exceeded the RCRA criterion for cadmium, and 67 percent (4 out of 6) of the TCLP leachates failed the RCRA criterion for lead. The maximum TCLP leachate concentrations for cadmium and lead were 17.2 mg/L and 15.2 mg/L, respectively. The combined bottom/fly ash and bottom ash TCLP leachate results showed that 25 percent (1 out of 4) of the leachates exceeded the RCRA criterion for cadmium, and 75 percent (3 out of 4) of the leachates exceeded the RCRA criterion for lead. The maximum TCLP leachate concentrations for cadmium and lead in the combined ash and bottom ash were 3.32 mg/L and 30.1 mg/L, respectively. The metals concentrations in the TCLP leachates of fly ash, combined ash, and bottom ash were below the RCRA criteria for arsenic, chromium, mercury, and selenium. Additionally, the metals concentrations in the natural field leachates were below the RCRA criteria for all six metals.

The analytical results for the ground-water samples metals concentrations (see Table 4.11) were compared to the primary and secondary drinking water standards. This comparison showed that all of the ground-water samples contained concentrations significantly below the primary and secondary drinking water standards for all metals except cadmium. One ground-water sample (monitoring well 2 at Facility B) had a cadmium concentration (0.0081 mg/L) that was only slightly below the primary drinking water standard (0.01 mg/L).

### 5.4.2 Polychlorinated Biphenyls

The EPA (TSCA) classifies solid materials containing PCBs as follows. If the solid material contains less than 50 parts per million (ppm) PCBs, it is considered to be non-hazardous and is not a regulated waste. Solid materials containing between 50 ppm and 500 ppm PCBs must be handled and disposed as "PCB-containing" materials. Finally, solid materials containing greater than 500 ppm PCBs must be handled and disposed as hazardous PCB waste materials. The PCB analyses of fly ash, bottom ash, and combined ash (see Table 4.6) in this study showed that the residues would not be regulated by TSCA based on their PCB content. The maximum PCB concentration for a fly ash sample was 24.77 ng/g (parts per billion), and the maximum PCB concentration for a bottom ash or combined ash sample was 32.15 ng/g. The maximum PCB concentration measured in this study was 375.5 ng/g for a landfill perimeter composite sample. The field water samples contained negligible concentrations of PCBs.

### 5.4.3 Polychlorinated Dibenzo-p-dioxins

The National Center for Disease Control has established a level of 1.0 part per billion (ppb) 2,3,7,8-TCDD in solid materials as the acceptable limit. The analytical results of the solid MWC residue samples for PCDDs (see Table 4.7) showed that this limit was occasionally exceeded. Twenty-seven percent (6 out of 23) of the fly ash samples contained 2,3,7,8-TCDD concentrations above 1.0 ppb, with a maximum concentration of 3.9 ppb. Therefore, these materials may be classified as potentially hazardous wastes and should be treated accordingly. Interestingly, all six of the samples exceeding the 1.0 ppb 2,3,7,8-TCDD limit were collected at Facility C. Although there are not any established standards or criteria for total PCDDs, several of the fly ash samples (8 out of 22) had PCDD concentrations greater than 1,000 ppb (1.0 ppb), with a maximum PCDD concentration of 12,018 ppb (12.0 ppm).

The results for the combined ash, bottom ash, and landfill perimeter composite samples were below the 1.0 ppb 2,3,7,8-TCDD limit, with a maximum 2,3,7,8-TCDD concentration of 0.78 ppb. Similarly, the PCDD concentrations for the field water and laboratory-prepared leachate samples were negligible, with a maximum 2,3,7,8-TCDD concentration of 0.17 ppb and a maximum total PCDD concentration of 2.55 ppb. This second observation indicates that the PCDDs vigorously adhere to the solid particles and are not mobile in the natural environment.

## 6.0 CONCLUSIONS

The objective of this study was to collect residues from four municipal waste combustor facilities for chemical characterization. In order to meet this objective, a step-by-step approach was established. First, the four MWC facilities were selected based on the criteria described in Section 3.1.1. Second, the facilities were visited, and the procedures detailed in Section 3.3 were used to collect the following samples: fly ash, bottom ash or combined bottom/fly ash, disposed ash (i.e., landfill perimeter composite), quench water, ground water, and field leachates. Additionally, laboratory leachates were prepared from the fly ash and the bottom ash or combined ash samples using the EP, TCLP, and MWEP (SW-924) procedures. Third, these samples were analyzed for metals, PCBs, PCDD/PCDFs, and organic constituents (i.e., total organic carbon, organic scan, and BNAs) using the procedures outlined in Section 3.4. Finally, the analytical data was compiled, summarized, and evaluated. The following conclusions were drawn from the results and discussion presented in Section 4.0 and the evaluation provided in Section 5.0.

1. The RCRA Maximum Allowable Concentration for cadmium was exceeded by 100 percent of the EP-prepared fly ash samples. However, the cadmium criterion was not exceeded by any of the EP-prepared combined ash or bottom ash leachates.

2. The RCRA Maximum Allowable Concentration for lead was exceeded by 83 percent of the EP-prepared fly ash leachates and by 75 percent of the EP-prepared combined ash or bottom ash leachates.

3. The concentrations of metals in the ground-water samples did not exceed the primary or secondary drinking water standards. This suggests that the natural leachates from the landfill have not had a major, adverse impact on the ground water.

4. The PCB concentrations were less than the 50 ppm limit established by TSCA for all solid samples. Therefore, the solid residues would not be classified as hazardous materials based solely on their PCB content.

5. The 2,3,7,8-TCDD concentration exceeded the limit of 1.0 ppb established by the National Center for Disease Control in 27 percent of the fly ash samples. This limit was not exceeded by any of the combined ash or bottom ash samples.

6. The variability of the contaminant concentrations between days, shifts, and units at any given facility was significant, indicating that slight changes in the incinerator feed material (i.e., the raw refuse) and/or the operating parameters significantly effected the quality of MWC residue. The variability of the contaminant concentrations between the facilities was extremely large (i.e., the standard deviations of the concentrations exceeded the average concentrations). This suggests that the variability of operating characteristics, facility design, and feed material composition between facilities has a significant impact on the resultant MWC residue quality.

7. In general, the weight ratio of bottom ash to fly ash was approximately 3 to 1 for the four facilities in this study.

8. The quench water at all four facilities was discharged to the local wastewater treatment plant. Based on the analytical results for the quench water samples, this appeared to be an acceptable disposal technique, because uncontrolled discharges of quench water to the environment should be prevented.

9. None of the four facilities had a functioning leachate collection and/or treatment system. However, the landfill at Facility A was designed and operated to minimize the contact between the waste and the environment, thereby reducing the potential for uncontrolled leachate discharges. The other three facilities did not control the discharges of natural field leachate.

10. There did not appear to be any correlation between the operating characteristics of the facilities and the metals concentrations in the residues.

11. The PCB and PCDD concentrations in the solid residues increased with decreasing incinerator temperature. Conversely, the PCDF concentration increased with increasing incinerator temperature.

12. The PCB concentrations in the solid residues were the highest for the water-wall grate incinerators (Facilities B and D), but the PCDD and PCDF concentrations were the highest for the combination reciprocating grate/rotary kiln incinerator (Facility C) and were lowest for the two water-wall grate facilities.

13. The fly ash contained higher concentrations of all metals except copper and iron than the bottom ash. Therefore, combining the ash fractions effectively diluted the total metals concentrations of the fly ash.

14. The fly ash consistently contained higher concentrations of PCBs, PCDDs, and PCDFs than the combined ash or bottom ash. However, the combined ash and bottom ash had higher concentrations of BNAs than the fly ash.

15. The concentrations of the predominant BNA compounds in the residues were generally near or below the detection limits.

16. The EP and TCLP methods were more aggressive than the MWEP (SW-924) method for extracting metals. The EP method appeared to be slightly more efficient than the TCLP method for leaching lead; however, the TCLP method appeared to be slightly more efficient than the EP method for extracting arsenic, chromium, and manganese. The extraction efficiencies of the EP and TCLP methods were approximately equal for the other metals. None of the laboratory leaching procedures were efficient for extracting organic compounds.

17. The results of the EP and TCLP leachate analyses approximated the natural field leachate analytical results for chromium, copper, iron, nickel, arsenic, mercury, and selenium. The SW-924 leachate concentrations for cadmium, lead, manganese, and zinc approximated the natural field leachate concentrations.

18. The leachable fraction of the total copper appeared to be inherent in the fly ash, and the leachable fractions of the total chromium, lead, manganese, nickel, and zinc appeared to be inherent in the bottom ash.

19. The contaminant concentrations of the disposed ash (i.e., the landfill perimeter composites) and the combined ash were not significantly different. This suggests that the concentration of the soluble (i.e., leachable) fraction of the contaminants compared to the total constituent concentrations is minimal.

20. The concentrations of PCBs, PCDDs, PCDFs, and BNAs were negligible in the field water and laboratory-prepared leachate samples. Therefore, these compounds appear to be relatively immobile in the natural environment.

21. The QA/QC objectives for sampling and analysis in this study were generally achieved. Although EPA/EMSL is currently improving the analytical method for PCBs in ash samples, some problems (e.g., low surrogate spike recovery) were encountered with these analyses.

22. All of the data generated in this study was comparable to the results from previous studies.

23. The Toxicity Characteristic Leaching Procedure (TCLP) was ineffective for extracting the organic constituents including PCDDs, PCDFs, and BNAs.

# APPENDIX A

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# APPENDIX B

# ANALYTICAL METHODS FOR PCDD/PCDFs

# ANALYTICAL PROCEDURES TO ASSAY STACK EFFLUENT SAMPLES AND RESIDUAL COMBUSTION PRODUCTS FOR POLYCHLORINATED DIBENZO-p-DIOXINS (PCDD) AND POLYCHLORINATED DIBENZOFURANS (PCDF)

## 1. Scope and Applicability of Method

The analytical procedures described here are applicable for the determination of polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) in stack effluents from combustion processes. These methods are also applicable to residual combustion products such as bottom and precipitator ash. The methods presented entail addition of isotopically-labeled internal standards to all samples in known quantities, extraction of the sample with appropriate organic solvents, preliminary fractionation and cleanup of the extracts using a sequence of liquid chromatography columns, and analysis of the processed extract for PCDD and PCDF using coupled gas chromatography - mass spectrometry (GC-MS). Various performance criteria are specified herein which the analytical data must satisfy for quality assurance purposes. These represent minimum criteria which must be incorporated into any program in which PCDD and PCDF are determined in combustion product samples.

The method presented here does not yield definitive information on the concentration of individual PCDD/PCDF isomers, except for 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD) and 2,3,7,8-Tetrachlorodibenzofuran (TCDF). Rather, it is designed to indicate the total concentration of the isomers of several chlorinated classes of PCDD/PCDF (that is, total tetra-, penta-, hexa-, hepta-, and octachlorinated dibenzo-p-dioxins and dibenzofurans). Of the 75 separate PCDD and 135 PCDF isomers, there are 22 TCDD, 38 TCDF, 14 PeCDD, 28 PeCDF, 10 HxCDD, 16 HxCDF, 2 HpCDD, 4 HpCDF, 1 OCDD and 1 OCDF.[a]

The analytical method presented herein is intended to be applicable for determining PCDD/PCDF present in combustion products at the ppt to ppm level, but the sensitivity which can ultimately be achieved for a given sample will depend upon the types and concentrations of other chemical compounds in the sample.

The method described here must be implemented by or under the supervision of chemists with experience in handling supertoxic materials and analyses should only be performed in rigorously controlled, limited access laboratories. The quantitation of PCDD/PCDF should be accomplished only by analysts experienced in utilizing capillary-column gas chromatography-mass spectrometry to accomplish quantitation of chlorocarbons and similar compounds at very low concentration.

The toxicological data which are available for the PCDD and PCDF are far from complete. That is, the toxicological properties of all of the isomers comprising the 75 possible PCDD and 135 possible PCDF are not presently known. However, a considerable body of toxicological data exists for 2,3,7,8-TCDD which indicates that, in certain animal species, this compound is lethal at extraordinarily low does and causes a wide range of systemic affects, including hepatic disorders, carcinoma and birth defects. While much less data is available regarding the toxicology of 2,3,7,8-TCDF, sufficient data is available to form the basis for the belief that 2,3,7,8-TCDF is similar in its toxicological properties to 2,3,7,8-TCDD. Relatively little is known about the toxicology of the higher chlorinated PCDD and PCDF (that is, penta through octachlorinated PCDD/PCDF), although there is some data to suggest that certain penta-, hexa-, and hepta- PCDD/PCDF isomers are hazardous. In view of the extraordinary toxicity of 2,3,7,8-TCDD and in view of the exceptional biological activity of this compound (on the basis of enzyme induction assays ) and of compounds having similar molecular structures, extensive precautions are required to preclude exposure to personnel during handling and analysis of materials containing these compounds and to prevent contamination of the laboratory. Specific safety and handling procedures which are recommended are given in the Appendix to this protocol.

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a. The abbreviations which are used to designate chlorinated dibenzo-p-dioxins and dibenzofurans throughout this document are as follows:

PCDD - Any or all of the 75 possible chlorinated dibenzo-p-dioxin isomers

PCDF - Any or all of the 135 possible chlorinated dibenzofuran isomers

TCDD - Any or all of the 22 possible tetrachlorinated dibenzo-p-dioxin isomer

TCDF - Any or all of the 138 possible tetrachlorinated dibenzofuran isomers

PeCDD - Any or all of the 14 possible pentachlorinated dibenzo-p-dioxin isome

PeCDF - Any or all of the 28 possible pentachlorinated dibenzofuran isomers

HxCDD - Any or all of the 10 possible hexachlorinated dibenzo-p-dioxin isomer

HXCDF - Any or all of the 16 possible hexachlorinated dibensofuran isomers

HpCDD - Any or all of the 2 possible heptachlorinated dibenzo-p-dioxin isomer

HpCDF - Any or all of the 4 possible heptachlorinated dibenzofuran isomers

OCDD - Octachlorodibenzo-p-dioxin

OCDF - Octachlorodibenzofuran

Specific Isomers. - Any of the abbreviations cited above may be converted to designate a specific isomer by indicating the exact positions (carbon atoms) where chlorines are located within the molecule. For example, 2,3,7,8-TCDD refers to only one of the 22 possible TCDD isomers - that isomer which is chlorinated in the 2,3,7,8 positions of the dibenzo-p-dioxin ring structure.

## 2. Reagents and Chemicals

The following reagents and chemicals are appropriate for use in these procedures. In all cases, equivalent materials from other suppliers may also be used.

2.1 Potassium Hydroxide, Anhydrous, Granular Sodium Sulfate and Sulfuric Acid (all Reagent Grade): J. T. Baker Chemical Co. or Fisher Scientific Co. The granular sodium sulfate is purified prior to use by placing a beaker containing the sodium sulfate in a 400°C oven for four hours, then removing the beaker and allowing it to cool in a desiccator. Store the purified sodium sulfate in a bottle equipped with a Teflon-lined screw cap.

2.2 Hexane, Methylene Chloride, Benzene, Methanol, Toluene, Isooctane: "Distilled in Glass" Burdick and Jackson.

2.3 Tridecane (Reagent Grade): Sigma Chemical Co.

2.4 Basic Alumina (Activity Grade 1, 100 - 200 mesh): ICN Pharmaceuticals. Immediately prior to use, the alumina is activated by heating for at least 16 hours at 600°C in a muffle furnace and then allowed to cool in a desiccator for at least 30 minutes prior to use. Store pre-conditioned alumina in a desiccator.

2.5 Silica (Bio-Sil A.100/200 mesh): Bio-Rad. The following procedure is recommended for conditioning the Bio-Sil A prior to use. Place an appropriate quantity of Bio-Sil A in a 30 mm x 300 mm long glass tube (the silica gel is held in place by glass wool plugs) which is placed in a tube furnace. The glass tube is connected to a pre-purified nitrogen cylinder, through a series of four traps (stainless steel tubes, 1.0 cm O.D. x 10 cm long)[6]: 1) Trap No. 1 - Mixture comprised of Chromosorb W/AW (60/80 mesh coated with 5% Apiezon L), Graphite (UCP-1-100), Activated Carbon (50 to 200 mesh) in a 7:1.5:1.5 ratio (Chromosorb W/AW, Apiezon L obtained from Supelco, Inc., Graphite obtained from Ultracarbon Corporation, 100 mesh, 1-M-USP; Activated Carbon obtained from Fisher Scientific Co.); 2) Trap No. 2 - Molecular Sieve 13 X (60/80 mesh), Supelco, Inc.; 3) Trap No. 3 - Carbosieve S (80/100 mesh), obtained from Supelco, Inc.; 4) The Bio-Sil A is heated in the tube for 30 minutes at 180°C while purging with nitrogen (flow rate 50-100 mL/minute), and the tube is then removed from the furnace and allowed to cool to room temperature. Methanol (175 mL) is then passed through the tube, followed by 175 mL methylene chloride. The tube containing the silica is then returned to the furnace, the nitrogen purge is again established (50-100 mL flow) and the tube is heated at 50°C for 10 minutes, then the temperature is gradually increased to 180°C over 25 minutes and maintained at 180°C for 90 minutes. Heating is then discontinued but the nitrogen purge is continued until the tube cools to room temperature. Finally, the silica is transferred to a clean, dry, glass bottle and capped with a Teflon-lined screw cap for storage.

2.6 Silica Gel Impregnated With Sulfuric Acid: Concentrated sulfuric acid (44 g) is combined with 100 g Bio-Sil A (conditioned as described above) in a screw capped bottle and agitated to mix thoroughly. Aggregates are dispersed with a stirring rod until a uniform mixture is obtained. The $H_2SO_4$-silica gel is stored in a screw-capped bottle (Teflon-lined cap).

2.7 Silica Gel Impregnated with Sodium Hydroxide: 1N Sodium hydroxide (39 g) is combined with 100 g Bio-Sil A (conditioned as described above) in a screw capped bottle and agitated to mix throughly. Aggregates are dispersed with a stirring rod until a uniform mixture is obtained. The NaOH-silica gel is stored in a screw-capped bottle (Teflon-lined cap).

2.8 Carbon/Celite:
Carbon: Amoco PX-21
Celite 545: Fisher Scientific Co

Combine Amoco PX-21 carbon (10.7 g) with Celite 545 (124 g) in a 250 mL glass bottle fitted with a Teflon-lined cap. Agitate the mixture to combine thoroughly. Store in the screw-capped bottle.

2.9 Sepralyte Diol (40µ): Analytichem International

2.10 Nitrogen and Hydrogen (Ultra High Purity): Matheson Scientific

## 3. Apparatus and Materials

The following apparatus and materials are appropriate for use in these procedures. In all cases, equivalent items from other suppliers may also be used.

3.1 Glassware used in the analytical procedures (including the Soxhlet apparatus and disposable bottles) is cleaned by rinsing successively three times with methanol and then three times with methylene chloride, and finally drying it in a 100°C oven. Bottles cleaned in this manner are allowed to cool to room temperature and are then capped using Teflon-lined lids. Teflon cap liners are rinsed as just described but are allowed to air-dry. More rigorous cleaning of some glassware with detergent may be required prior to the solvent rinses, for example, the glassware employed for Soxhlet extraction of samples.

3.1.1 Sample Vessels: 125 mL and 250 mL flint glass bottles fitted with screw caps and teflon cap liners, and glass test tubes, VWR-Scientific.

3.1.2 Teflon Cap Liners: Scientific Specialities Service, Inc.

3.1.3 Soxhlet Apparatus: Extraction apparatus, Allihn condenser, Kimax Brand, American Scientific Products Cat. No. E6252-2A.

3.1.4 Gravity Flow Liquid Chromatographic Columns: Custom Fabricated (Details of the columns are provided in later sections).

3.1.5 Micro-vials (3.0 mL): Reliance Glass.

3.2 Capillary Gas Chromatographic Columns: Two different columns are required if data on both 2,3,7,8-TCDD and 2,3,7,8-TCDF, as well as on the total PCDD/PCDF by chlorinated class, are desired. The appropriate columns are: 1) A fused silica column (60 M x 0.25 mm I.D.) coated with DB-5 (0.25 u film thickness), J & S Scientific, Inc., Crystal Lake, IL is utilized to separate each of the several tetra-through octachlorinated CDDs and CDFs, as a group, from all of the other groups. While this column does not resolve all of the isomers within each chlorinated group, it effectively resolves each of the chlorinated groups from all of the other chlorinated groups and therefore provides data on the total concentration of each group (that is, total tetra-, penta-, hexa-, hepta- and octa CDDs and CDFs). This column also resolves 2,3,7,8-TCDD from all of the other 21 TCDD isomers and this isomer can therefore be determined quantitatively if proper calibration procedures are applied as described further in a later section. This column does not completely resolve 2,3,7,8-TCDF from the other TCDF isomers, and if a peak corresponding in retention time to 2,3,7,8-TCDF is observed in the analysis using this column, then a portion of the sample extract must be reanalyzed using the second GC column described below if isomer - specific data on 2,3,7,8-TCDF is desired. 2) A fused silica column (30 M x 0.25 mm I.D.) coated with DB-225 (0.25 u film thickness), J & S Scientific, Inc., Crystal Lake, IL, must be utilized to obtain quantitative data on the concentration of 2,3,7,8-TCDF, since this column adequately resolves 2,3,7,8-TCDF from the other TCDF isomers.

3.3 Balance: Analytical Balance, readibility, 0.0001 g.

3.4 Nitrogen Blowdown Concentration Apparatus: N-Evap Analytical Evaporator Model III, Organomation Associates Inc.

3.5 Tube Furnace: Lindberg Type 59344.

## 4. Instrumentation

Gas Chromatograph-Mass Spectrometer-Data System (GC/MS/DS): The instrument system used to analyze sample extracts for PCDD/PCDF comprises a gas chromatograph (fitted for capillary columns) coupled directly or through an enrichment device to a mass spectrometer which is equipped with a computer-based data system. The individual components of the GC/MS/DS are described below.

4.1 Gas Chromatograph (GC): The chromatograph must be equipped with an appropriate injector and pneumatic system to permit use of the specified glass or fused silica capillary columns. It must also incorporate an oven which can be heated in a reproducible, programmed temperature cycle. The injector should be configured for splitless/split injections. The GC column performance should be verified at the beginning of each 8 hour work period or at the beginning of each series of analyses if more than one set of samples is analyzed during an 8 hour shift. Extracts of complex combustion products and effluents may contain numerous organic residues even after application of the extensive prefractionation/cleanup procedures specified in this method. These residues may result in serious deviation of GC column performance and therefore, frequent performance checks are desirable. Using appropriate calibration mixtures, as described below, the retention time windows for each chlorinated class of CDDs/CDFs must be verified. In addition, the GC column utilized must be demonstrated to effectively separate 2,3,7,8-TCDD from all other TCDD isomers if data on 2,3,7,8-TCDD alone is desired with at least 20% valley definition between the 2,3,7,8- isomer and the other adjacent-eluting TCDD isomers. Typically, capillary column peak widths (at half-maximum peak height) on the order of 5-10 seconds are obtained in the course of these analyses. An appropriate GC temperature program for the analyses described herein is discussed in a later section (see Table 1).

4.2 Gas Chromatograph-Mass Spectrometer Interface: The GC-MS interface can include enrichment devices, such as a glass jet separator or a silicone membrane separator, or the gas chromatograph can be directly coupled to the mass spectrometer source, if the system has adequate pumping of the source region. The interface may include a diverter valve for shunting the column effluent and isolating the mass spectrometer source. All components of the interface should be glass or glass-lined stainless steel. The interface components must be compatible with temperatures in the neighborhood of 250°C, which is the temperature at which the interface is typically maintained throughout analyses for PCDD/PCDF. The GC/MS interface must be appropriately configured so that the separation of 2,3,7,8-TCDD from the other TCDD isomers which is achieved in the gas chromatographic column is not appreciably degraded. Cold spots and/or active surfaces (adsorption sites) in the GC/MS interface can cause peak tailing and peak broadening. If the latter are observed, thorough cleaning of the injection port, interface and connecting lines should be accomplished prior to proceeding.

4.3 Mass Spectrometer (MS): The mass spectrometer used for the analyses described here is typically a double-focusing sector or quadrupole instrument equipped with an electron impact source (70 ev), maintained at 250°C, and a standard electron multiplier detector. If possible, it is desirable to have both low and high resolution capability with the mass spectrometer used, since confirmation of data obtained by low resolution MS using high resolution MS is sometimes desirable. Alternatively, a combination of mass spectrometers can be used for this purpose. The static resolution of the instrument must be maintained at a minimum of 1:500 (with a 10% valley between adjacent masses) if operating in the low resolution MS mode, and a minimum resolution of 1:10,000 is desirable for operation in the high resolution mode. The mass spectrometer must also be configured for rapid computer-controlled selected-ion monitoring in both high and low resolution operating modes. At a minimum, two ion-masses characteristic of each class of chlorinated dioxins should be monitored, and these are two ions in the molecular ion isotopic cluster. It is desirable for increased confidence in the data to also monitor the fragment ions arising from the loss of COCl from the molecular ion. In order to accomplish the requisite rapid multiple ion monitoring sequence during the time period defined by a typically capillary chromatographic peak (the base of the chromatographic peak is typically 15-20 seconds in width), the following MS performance parameters are typically required (assuming a 4-ion monitoring sequence for each class of PCDD/PCDF): dwell time/ion-mass, ≤100 msec.; minimum number of data points/chromatographic peak, 7 . The mass scale of the mass spectrometer is calibrated using high boiling perfluorokerosene and/or some other suitable mass standard depending upon the requirements of the GC-MS-DS system utilized. The actual procedures utilized for calibration of the mass scale will be unique to the particular mass spectrometer being employed. A list of the appropriate ions to be monitored in the PCDD/PCDF analyses described herein is presented in a later section (see Table 1).

4.4 Data System: A dedicated computer-based data system, capable of providing the data described above, is employed to control the rapid selected-ion monitoring sequence and to acquire the data. Both digital data (peak areas or peak heights) as well as peak profiles (displays of intensities of ion-masses monitored as a function of time) should be acquired during the analyses, and displayed by the data system. This raw data (mass chromatograms) should be provided in the report of the data.

## 5. Calibration Standards

A recommended set of calibration standards to be used in the analyses described herein is presented below. Stock standard solutions of the various PCDD and PCDF isomers and mixtures thereof are prepared in a glovebox, using weighed quantities of the authentic isomers.[b] These stock solutions are contained in appropriate volumetric flasks and are stored tightly stoppered, in a refrigerator. Aliquots of the stock standards are removed for direct use or for subsequent serial dilutions to prepare working standards. These standards must be checked regularly (by comparing instrument response factors for them over a period of time) to ensure that solvent evaporation or other losses have not occurred which would alter the standard concentration. The several recommended standard solutions are as follows.

5.1 Standard Mixture A: Prepare a stock solution containing the following isotopically-labelled PCDD and PCDF in isooctane at the indicated concentrations: 2.5ng./µl $^{13}C_{12}$-2,3,7,8-TCDD, 2.5ng/µl $^{37}Cl_4$-2,3,7,8-TCDF, 25ng/µL $^{13}C_{12}$-1,2,3,4,7,8-HxCDD, 25ng/µL $^{13}C_{12}$-1,2,3,4,7,8-HxCDF, 25ng/µL $^{13}C_{12}$-OCDD, and 25ng/µL $^{13}C_{12}$-OCDF. Portions of this isomer mixture are added to all samples prior to analyses and serve as internal standards for use in quantitation. Recovery of these standards is also used to guage the overall efficacy of the analytical procedures.

5.2 Standard B: Prepare a stock solution containing 1.0 ng of $^{37}Cl_4$-2,3,7,8-TCDD/µL of isooctane. This standard can be coinjected if desired, along with aliquots of the final sample extract to reliably estimate the recovery of the $^{13}C_{12}$-2,3,7,8-TCDD surrogate standard.

5.3 Standard Mixture C: Prepare a stock solution containing 100 ng/µL of isooctane of each of the following PCDD and PCDF: 2,3,7,8-TCDF; 2,3,7,8-TCDD; 1,3,4,6,8-PeCDF, 2,3,4,6,7-PeCDF; 1,2,4,7.9-PeCDD; 1,2,3,8,9-PeCDD; 1,2,3,4,6,8-HxCDF; 2,3,4,6,7,8-HxCDF; 1,2,3,4,6,8-HxCDD, 1,2,3,4,6,7-HxCDD; 1,2,3,4,6,7,8-HpCDF; 1,2,3,4,7,8,9-HpCDF; 1,2,3,4,6,7,8-HpCDD; 1,2,3,4,6,7,9-HpCDD; OCDF: and OCDD. This isomer mixture is used to define the gas chromatographic retention time intervals or windows for each of the penta-, hexa-, hepta-, and octachlorinated groups of PCDD and PCDF. Each pair of isomers of a given chlorinated class which is listed here corresponds to the first and last eluting isomers of that class on the DB-5 capillary GC column (except for TCDD and TCDF). In addition, this isomer mixture is used to determine GC-MS response factors for representative isomers of each of the penta-, hexa-, hepta-, and octachlorinated groups of PCDD and PCDF. The later data are used in quantitating the analytes in unknown samples.

5.4 Standard Mixture D: Prepare a stock solution containing 50 pg/µL of isooctane of each of the following TCDD isomers: 1,3,6,8-TCDD; 1,2,3,7-TCDD; 1,2,3,9-TCDD; 2,3,7,8-TCDD; and 1,2,8,9-TCDD. Two of the isomers in this mixture are used to define the gas chromatographic retention time window for TCDDs (1,3,6,8-TCDD is the first eluting TCDD

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[b] Some of the PCDD/PCDF isomer standards recommended for this method are available from Cambridge Isotope Laboratories, Cambridge, Massachusetts. Other PCDD/PCDF standards are available from the Brehm Laboratory, Wright State University, Dayton, Ohio, from the U.S. EPA Standard Repository at Research Triangle Park, North Carolina and possibly from other laboratories. Not all of the indicated isotopically-labelled PCDD/PCDF internal standards recommended here are presently available in quantities sufficient for widespread distribution, but these are expected to be available in the near future.

time) to ensure that solvent evaporation or other losses have not occurred which would alter the standard concentration. The several recommended standard solutions are as follows.

5.1 Standard Mixture A: Prepare a stock solution containing the following isotopically-labelled PCDD and PCDF in isooctane at the indicated concentrations: 2.5ng./ul $^{13}C_{12}$-2,3,7,8-TCDD, 2.5ng/ul $^{37}Cl_4$-2,3,7,8-TCDF, 25ng/uL $^{13}C_{12}$-1,2,3,4,7,8-HxCDD, 25ng/uL $^{13}C_{12}$-1,2,3,4,7,8-HxCDF, 25ng/uL $^{13}C_{12}$-OCDD, and 25ng/uL $^{13}C_{12}$-OCDF. Portions of this isomer mixture are added to all samples prior to analyses and serve as internal standards for use in quantitation. Recovery of these standards is also used to guage the overall efficacy of the analytical procedures.

5.2 Standard B: Prepare a stock solution containing 1.0 ng of $^{37}Cl_4$-2,3,7,8-TCDD/uL of isooctane. This standard can be coinjected if desired, along with aliquots of the final sample extract to reliably estimate the recovery of the $^{13}C_{12}$-2,3,7,8-TCDD surrogate standard.

5.3 Standard Mixture C: Prepare a stock solution containing 100 ng/uL of isooctane of each of the following PCDD and PCDF: 2,3,7,8-TCDF; 2,3,7,8-TCDD; 1,3,4,6,8-PeCDF, 2,3,4,6,7-PeCDF; 1,2,4,7.9-PeCDD; 1,2,3,8,9-PeCDD; 1,2,3,4,6,8-HxCDF; 2,3,4,6,7,8-HxCDF; 1,2,3,4,6,8-HxCDD, 1,2,3,4,6,7-HxCDD; 1,2,3,4,6,7,8-HpCDF; 1,2,3,4,7,8,9-HpCDF; 1,2,3,4,6,7,8-HpCDD; 1,2,3,4,6,7,9-HpCDD; OCDF: and OCDD. This isomer mixture is used to define the gas chromatographic retention time intervals or windows for each of the penta-, hexa-, hepta-, and octachlorinated groups of PCDD and PCDF. Each pair of isomers of a given chlorinated class which is listed here corresponds to the first and last eluting isomers of that class on the DB-5 capillary GC column (except for TCDD and TCDF). In addition, this isomer mixture is used to determine GC-MS response factors for representative isomers of each of the penta-, hexa-, hepta-, and octachlorinated groups of PCDD and PCDF. The later data are used in quantitating the analytes in unknown samples.

5.4 Standard Mixture D: Prepare a stock solution containing 50 pg/uL of isooctane of each of the following TCDD isomers: 1,3,6,8-TCDD; 1,2,3,7-TCDD; 1,2,3,9-TCDD; 2,3,7,8-TCDD; and 1,2,8,9-TCDD. Two of the isomers in this mixture are used to define the gas chromatographic retention time window for TCDDs (1,3,6,8-TCDD is the first eluting TCDD

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[b] Some of the PCDD/PCDF isomer standards recommended for this method are available from Cambridge Isotope Laboratories, Cambridge, Massachusetts. Other PCDD/PCDF standards are available from the Brehm Laboratory, Wright State University, Dayton, Ohio, from the U.S. EPA Standard Repository at Research Triangle Park, North Carolina and possibly from other laboratories. Not all of the indicated isotopically-labelled PCDD/PCDF internal standards recommended here are presently available in quantities sufficient for widespread distribution, but these are expected to be available in the near future.

isomer and 1,2,8,9-TCDD is the last eluting TCDD isomer on the DB-5 GC column). The remaining isomers serve to demonstrate that the 2,3,7,8-TCDD isomer is resolved from the other nearest eluting TCDD isomers, and that the column therefore yields quantitative data for the 2,3,7,8-TCDD isomer alone.

5.5 Standard Mixture E: Prepare a stock solution containing 50 pg/uL of isooctane of each of the following TCDF isomers: 1,3,6,8-TCDF; 2,3,4,8-TCDF; 2,3,7,8-TCDF, 2,3,4,7-TCDF; and 1,2,8,9-TCDF. This isomer mixture is used to define the TCDF gas chromatographic retention time window (1,3,6,8- and 1,2,8,9-TCDF are the first and last eluting TCDFs on the DB-5 capillary column) and to demonstrate that 2,3,7,8-TCDF is uniquely resolved from the adjacent-eluting TCDF isomers.

## 6. Procedures for Addition of Internal Standards and Extraction of Samples

Both liquid and solid samples will be obtained for PCDD/PCDF analyses as a result of the application of an appropriate stack sampling procedure. Samples resulting from the sampling train will include the following (these will be provided to the analytical laboratory as separate samples in the form indicated): 1) particulate filter and particulates thereon; 2) particulates from the cyclone (if used); 3) combined aqueous solutions from the impingers; 4) the intact XAD-resin cartridge and the resin therein; 5) combined aqueous rinse (if used) solutions from rinses of the nozzle, probe, filter holder, cyclone (if used), impingers, and all connecting lines; 6) combined acetone rinse solutions from rinses of the nozzle, probe, filter holder, cyclone (if used), impingers, and all connecting lines; 7) combined hexane rinse solutions from rinses of the nozzle, probe, filter, cyclone (if used), impingers, and all connecting lines. In addition, samples of bottom ash, precipitator ash, incinerator feed materials or fuel, quench liquids, and materials from effluent control devices may also be provided for analyses.

In general, the volumes of all liquid samples received for analyses are measured and recorded, and where appropriate, solid samples or aliquots thereof are weighed. Any samples which are homogeneous (as for example, a single liquid phase sample or a solid which can be thoroughly mixed) can be split prior to analyses, if desired, provided that this will still permit the attainment of the desired detection limits for the analytes of interest. Samples such as particulates from the sampling train which are generally collected in relatively small quantity, are preferably analyzed in total.

6.1 Organic Liquid Samples (Acetone and Hexane Solutions) Concentrate each of the combined organic liquids (acetone and hexane solutions) to a volume of about 1-5 mL using the nitrogen blowdown apparatus (a stream of dry nitrogen) while heating the sample gently on a water bath. Pool the concentrated residues, rinsing the vessels three times with small portions of hexane and adding these to the residues, and concentrate to near dryness. This residue will likely contain particulates which were removed in the rinses of the train probe and nozzle. Combine the residue (along with three rinses of the final sample vessel) in the Soxhlet apparatus with the filter and particulates, and proceed as described under Solid Sample below.

### 6.2 Aqueous Liquids

Add an appropriate quantity of the isotopically-labeled internal standard mixture (Standard Mixture A described earlier) to the aqueous liquid sample (or an aliquot thereof) in a screw-capped bottle fitted with a Teflon-lined cap. Add approximately 25% by volume of hexane to the spiked aqueous sample, seal the bottle and agitate on a shaker for a period of three hours. Allow the vessel to stand until the aqueous and organic layers separate, then transfer the organic layer to a separate sample bottle. Repeat the hexane extraction sequence two additional times and combine the organic fractions with that from the first extraction. Proceed with the sample fractionation and cleanup procedures described below.

### 6.3 Solid Samples

Place a glass extraction thimble and 1 g of silica gel and a plug of glass wool into the Soxhlet apparatus, charge the apparatus with toluene and reflux for a period of one hour. Remove the toluene and discard it, retaining the silica gel, or if desired, retain a portion of the toluene to check for background contamination. For extraction of particulates, place the entire sample in the thimble onto the bed of precleaned silica gel (1 cm. thick), and top with the precleaned glass wool retained from the initial Soxhlet cleaning procedure. Add the appropriate quantity of the isotopically-labelled internal standard mixture (Standard Mixture A described earlier) to the sample in the Soxhlet thimble. Charge the Soxhlet with toluene and reflux for a period of 16 hours. After extraction, allow the Soxhlet to cool, remove the toluene extract, and transfer it to another sample vessel. Concentrate the extract to a volume of approximately 40 ml by using the nitrogen blowdown apparatus described earlier. Proceed with the sample fractionation and cleanup procedures described below.

## 7. Procedures for Cleanup and Fractionation of Sample Extracts

The following column chromatographic sample clean-up procedures are used in the order given, although not all may be required. In general, the silica and alumina column procedures are considered to be a minimum requirement. Acceptable alternative cleanup procedures may be used provided that they are demonstrated to effectively transmit a representative set of the analytes of interest. The column chromatographic procedures listed here have been demonstrated to be effective for a mixture consisting of 1,2,3,4-TCDD, 2,3,7,8-TCDD, 2,3,6,8-TCDF, 1,2,4,8-TCDF, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDD, 1,2,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDD, 1,2,4,6,7.9-HxCDF, 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,8,9-HpCDF, OCDD and OCDF

An extract obtained as described in the foregoing sections is concentrated to a volume of about 1 mL using the nitrogen blowdown apparatus, and this is transferred quantitatively (with rinsings) to the combination silica gel column described below.

7.1 Combination Silica Gel Column: Pack one end of a glass column (20 mm. O.D. x 230 mm in length) with glass wool (precleaned) and add, in sequence, 1 g silica gel, 2 g base-modified silica gel, 1 g silica gel, 4 g acid-modified silica gel, and 1 g silica gel. (Silica gel and modified silica gel are prepared as described in the Reagents sections of this protocol.) Preelute the column with 30 mL hexane and discard the eluate. Add the sample extract in 5 mL of hexane to the column along with two additional 5 ml rinses. Elute the column with an additional 90 mL of hexane and retain the entire eluate. Concentrate this solution to a volume of about 1 ml.

7.2 Basic Alumina Column: Cut off a 10 mL disposable Pasteur glass pipette at the 4 mL graduation mark and pack the lower section with glass wool (precleaned ) and 3 g of Woelm basic alumina (prepared as described in the Reagent section of this protocol). Transfer the concentrated extract from the combination silica column to the top of the column and elute the column sequentially with 15 mL of hexane, 10 mL of 8% methylene chloride-in-hexane and 15 mL of 50% methylene chloride-in-hexane, discarding the first two eluate fractions and retaining the third eluate fraction. Concentrate the latter fraction to about 0.5 mL using the nitrogen blowdown apparatus described earlier.

7.3 PX-21 Carbon/Celite 545 Column: Take a 9 inch disposable Pasteur pipette and cut off a 0.5 inch section from the constricted tip. Insert a filter paper disk at the top of the tube, 2.5 cm. from the constriction. Add a sufficient quantity of PX-21 Carbon/Celite 545 (Prepared as described in the reagent section of this protocol) to the tube to form a 2 cm. length of the Carbon-Celite. Insert a glass wool plug. Preelute the column in sequence with 2 mL of 50% benzene-in-ethyl acetate, 1 mL of 50% methylene chloride-in-cyclohexane and 2 mL of hexane, and discard these eluates. Load the extract (in 1 mL of hexane) from the alumina column onto the top of the column, along with 1 mL hexane rinse. Elute the column with 2 mL of 50% methylene chloride-in-hexane and 2 mL of 50% benzene-in-ethyl acetate and discard these eluates. Invert the column and reverse elute it with 4 mL of toluene, retaining this eluate. Concentrate the eluate and transfer it to a Reacti-Vial for storage. Store extracts in a freezer, shielded from light, prior to GC-MS analysis. If desired, still another column chromatographic clean-up step can be employed prior to concentration of the extract, as described below.

7.4 Silica/Diol Micro Column Cleanup: After the above clean-up steps small amounts of highly colored polar compounds may be present in complex samples. These are removed, if necessary, by the following column: Push a small plug of glass wool into a disposable 6 mm i.d. glass Pasteur pipette, followed by 3 mm of Sepralyte (Analytichem International), 6 mm of silica gel and finally 3 mm of sodium sulfate. The column is pre-wet with hexane, the sample is applied in 100 µL of 100% hexane and eluted with hexane, collecting 1.5 ml.

## 8. Procedure for Analysis of Sample Extracts for PCDD/PCDF Using Gas Chromatography-Mass Spectrometry (GC-MS).

8.1 Sample extracts prepared by the procedures described in the foregoing are analyzed by GC-MS utilizing the following instrumental parameters. Typically, 1 to 5 uL portions of the extract are injected into the GC. Sample extracts are first analyzed using the DB-5 capillary GC column to obtain data on the concentrations of total tetra-through octa-CDDs and CDFs, and on 2,3,7,8-TCDD. If tetra-CDFs are detected in this analysis, then another aliquot of the sample is analyzed in a separate run, using the DB-225 column to obtain data on the concentration of 2,3,7,8-TCDF.

### 8.2 Gas Chromatograph

8.2.1 Injector: Configured for capillary column, splitless/split injection (split flow on 60 seconds following injection), injector temperature, 250°C.

8.2.2 Carrier gas: Hydrogen, 30 lb head pressure.

8.2.3 Capillary Column 1: For total tetra- through octa - CDDs/CDFs and 2,3,7,8-TCDD, 60 M x 0.25 mm I.D. fused silica DB-5; temperature programmed (see Table 1 for temperature program). Capillary Column 2: for 2,3,7,8-TCDF only, 60 M x 0.25 mm I.D. fused silica DB-225, temperature programmed (180°C for 1 min., then increase from 180°C to 240°C @ 5°C/min., hold at 240°C for 1 min.)

8.2.4 Interface Temperature: 250°C

### 8.3 Mass Spectrometer

8.3.1 Ionization Mode: Electron impact (70 eV)

8.3.2 Static Resolution: 1:600 (10% valley) or 1:10,000 depending upon requirements. Usually the sample extracts are initially analyzed using low resolution MS, then if PCDD/PCDF are detected, it is desirable to analyze a second portion of the sample extract using high resolution MS.

8.3.3 Source Temperature: 250°C

8.3.4 Ions Monitored: Computer-Controlled Selected-Ion Monitoring, See Table 1 for list of ion masses monitored and time intervals during which ions characteristic of each class of CDDs and CDFs are monitored.

8.4 Calibration Procedures:

8.4.1 Calibrating the MS Mass Scale: Perfluoro Kerosene, decafluorotriphenyl phosphine, or any other accepted mass marker compound must be introduced into the MS, in order to calibrate the mass scale through at least m/z 500. The procedures specified by the manufacturer for the particular MS instrument used are to be employed for this purpose. The mass calibration should be rechecked at least at 8 hr. operating intervals.

8.4.2 Table 1 shows the GC temperature program typically used to resolve each chlorinated class of PCDD and PCDF from the other chlorinated classes, and indicates the corresponding time intervals during which ions indicative of each chlorinated class are monitored by the MS. This temperature program and ion monitoring time cycle must be established by each analyst for the particular instrumentation used by injecting aliquots of Standard Mixtures C, D. and E (See earlier section of this protocol for description of these mixtures). It may be necessary to adjust the temperature program and ion monitoring cycles slightly based on the observations from analysis of these mixtures.

8.4.3 Checking GC Column Resolution for 2,3,7,8-TCDD and 2,3,7,8-TCDF: Utilize the column-resolution TCDD and TCDF isomer mixtures (Standard Mixtures D and E, containing 50 pg/µl, respectively of the appropriate TCDD and TCDF isomers) to verify that 2,3,7,8-TCDD and 2,3,7,8-TCDF are separated from the other TCDD and TCDF isomers, respectively. A 20% valley or less must be obtained between the mass chromatographic peak observed for 2,3,7,8-TCDD and adjacent peaks arising from other TCDD isomers,and similar separation of 2,3,7,8-TCDF from other neighboring TCDFs,is required. Standard Mixture D is utilized with the DB5 column and Standard Mixture E with the DB-225 column. Analyze the column performance standards using the instrumental parameters specified in Sections 8.2 and 8.3, and in Table 1. The column performance evaluation must be performed each time a new column is installed in the gas chromatograph, and at least once during each 8 hour operating period. Providing that the same column is employed for a period of time, its performance can also be gauged by noting the peak width (at 1/2 peak height) for 2,3,7,8-TCDD or for 2,3,7,8-TCDF. If this peak width is observed to broaden by 20% or more as compared to the usual width for satisfactory operation, then the column resolution is suspect and must be checked. If the column resolution is found to be insufficient to resolve 2,3,7,8-TCDD and 2,3,7,8-TCDF from their neighboring TCDD and TCDF isomers, respectively, (as measured on the two different columns used for resolving these two isomers), then a new DB-5 and/or DB-225 GC column must be installed.

8.4.4 Calibration of the GC-MS-DS system to accomplish quantitative analysis of 2,3,7,8-TCDD and 2,3,7,8-TCDF, and of the total tetra- through octa-CDDs and CDFs contained in the sample extract, is accomplished by analyzing a series of at least three working calibration standards. Each of these standards is prepared to contain the same concentration of each of the stable-isotopically labelled internal standards used here (Standard Mixture A) but a different concentration of native PCDD/PCDF (Standard Mixture C). Typically, mixtures will be prepared so that the ratio of native PCDD and PCDF to isotopically-labelled PCDD and PCDF will be on the order of 0.1, 0.5 and 1.0 in the three working calibration mixtures. The actual concentrations of both native and isotopically-labelled PCDD and PCDF in the working calibration standards will be selected by the analyst on the basis of the concentrations to be measured in the actual sample extracts. At the time when aliquots of each of the standards are injected (and also when injecting aliquots of actual sample extracts), if desired, an aliquot of a standard containing typically 1 ng of $^{37}Cl_4$-2,3,7,8-TCDD (Standard B) can be drawn into the micro syringe containing the calibration solution described above (or the sample extract) and this is then co-injected along with the sample extract in order to obtain data permitting calculation of the percent recovery of the $^{13}C_{12}$-2,3,7,8-TCDD internal standard. Equations for calculating relative response factors from the calibration data derived from the calibration standard analyses, and for calculating the recovery of the $^{13}C_{12}$-2,3,7,8-TCDD and the other isotopically-labelled PCDD and PCDF, and the concentration of native PCDD and PCDF in the sample (from the extract analysis), are summarized below. In these calculations, as can be seen, 2,3,7,8-TCDD is employed as the illustrative model. However, the calculations for each of the other native dioxins and furans in the sample analyzed are accomplished in an analgous manner. It should be noted that in view of the fact that stable-isotopically labelled internal standards corresponding to each tetra- through octachlorinated class are not used here (owing to limited availability at this time) the following approach is adopted: For quantitation of tetrachlorinated dibenzofurans $^{13}C_{12}$-2,3,7,8-TCDF is used as the internal standard. For quantitation of tetrachlorodibenzo-p-dioxins, $^{13}C_{12}$-2,3,7,8-TCDD is used as the internal standard. For quantitation of PeCDD, HxCDD, PeCDF, and HxCDF, the corresponding stable-isotopically labelled HxCDD and HxCDF internal standards are used. For quantitation of HpCDD, OCDD, and HpCDF, OCDF, the isotopically-labelled OCDD and OCDF, respectively, are used. Inherent in this approach is the assumption that the response factors for each of the isomers of each chlorinated class are the same, and in the case of the penta- and hepta-CDDs and CDFs, the assumption is made that the responses for these two classes are equivalent to those for the tetra-isomers and the octa-isomers, respectively.

8.4.5 Equations for Calculating Response Factors, Concentration of 2,3,7,8-TCDD In An Unknown Sample, and Recoveries of Internal Standards.

Equation 1: Response Factor (RRF) for native 2,3,7,8-TCDD using $^{13}C_{12}$-2,3,7,8-TCDD as an internal standard.

$RRF_d = (A_s C_{is}/A_{is} C_s)$

where: $A_s$ = SIM response for 2,3,7,8-TCDD ion at m/z 320 + 322

$A_{is}$ = SIM response for $^{13}C_{12}$-2,3,7,8-TCDD internal standard ion at m/z 332

$C_{is}$ = Concentration of the internal standard (pg./uL.)

$C_s$ = Concentration of the 2,3,7,8-TCDD (pg./uL.)

Equation 2: Response Factor (RRF) for $^{37}Cl_4$-2,3,7,8-TCDD, the co-injected external standard

$RRF_f = (A_{is} C_{es})/(A_{es} C_{is})$

where: $A_{is}$ = SIM response for $^{13}C_{12}$-2,3,7,8-TCDD internal standard ion at m/z 332

$A_{es}$ = SIM response for co-injected $^{37}Cl_4$-2,3,7,8-TCDD external standard at m/z 328 - 0.009 (SIM response for native 2,3,7,8-TCDD at m/z 322)

$C_{is}$ = Concentration of the internal standard (pg./uL.)

$C_{es}$ = Concentration of the external standard (pg./uL.)

Equation 3: Calculation of concentration of native 2,3,7,8-TCDD using $^{13}C_{12}$-2,3,7,8-TCDD as internal standard

Concentration, pg./g. = $(A_s)\ (I_s)/(A_{is})(RRF_d)(W)$

where: $A_s$ = SIM response for 2,3,7,8-TCDD ion at m/z 320 + 322

$A_{is}$ = SIM response for the $^{13}C_{12}$-2,3,7,8-TCDD internal standard ion at m/z 332

$I_s$ = Amount of internal standard added to each sample (pg.)

$W$ = Weight of soil or waste in grams

$RRF_d$ = Relative response factor from Equation 1

Equation 4: Calculation of % recovery of $^{13}C_{12}$-2,3,7,8-TCDD internal standard

% Recovery = $100(A_{is})(E_s)/(A_{es})(I_1)(RRF_f)$

$A_{is}$ = SIM response for $^{13}C_{12}$-2,3,7,8-TCDD internal standard ion at m/z 332

$A_{es}$ = SIM response for $^{37}Cl_4$-2,3,7,8-TCDD external standard ion at m/z 328 - 0.009 (SIM Response for native 2,3,7,8-TCDD at m/z 322)

$E_s$ = Amount of $^{37}Cl_4$-2,3,7,8-TCDD external standard co-injected with sample extract (ng.)

$I_1$ = Theoretical amount of $^{13}C_{12}$-2,3,7,8-TCDD internal standard in injection

$RRF_f$ = Relative response factor from Equation 2

As noted above, procedures similar to these are applied to calculate analytical results for all of the other PCDD/PCDF determined in this method.

8.5 Criteria Which GC-MS Data Must Satisfy for Identification of PCDD/PCDF in Samples Analyzed and Additional Details of Calculation Procedures.

In order to identify specific PCDD/PCDF in samples analyzed, the GC-MS data obtained must satisfy the following criteria:

8.5.1 Mass spectral responses must be observed at both the molecular and fragment ion masses corresponding to the ions indicative of each chlorinated class of PCDD/PCDF identified (see Table 1) and intensities of these ions must maximize essentially simultaneously (within ± 1 second). In addition, the chromatographic retention times observed for each PCDD/PCDF signal must be correct relative to the appropriate stable-isotopically labelled internal standard and must be consistent with the retention time windows established for the chlorinated group to which the particular PCDD/PCDF is assigned.

8.5.2 The ratio of the intensity of the molecular ion $(M)^+$ signal to that of the $(M+2)^+$ signal must be within ± 10% of the theoretically expected ratio (for example, 0.77 in the case of TCDD; therefore the acceptable range for this ratio is 0.62 to 0.92).

8.5.3 The intensities of the ion signals are considered to be detectable if each exceeds the baseline noise by a factor of at least 3:1. The ion intensities are considered to be quantitatively measurable if each ion intensity exceeds the baseline noise by a factor of at least 5:1[c].

8.5.4 For reliable detection and quantitation of PCDF it is also desirable to monitor signals arising from chlorinated diphenyl ethers which, if present could give rise to fragment ions yielding ion masses identical to those monitored as indicators of the PCDF. Accordingly, in Table 1, appropriate chlorinated diphenyl ether masses are specified which must be monitored simultaneously with the PCDF ion-masses. Only when the response for the diphenyl ether ion mass is not detected at the same time as the PCDF ion mass can the signal obtained for an apparent PCDF be considered unique.

8.5.5 Measurement of the concentration of the congeners in a chlorinated class using the methods described herein is based on the assumption that all of the congeners are identical to the calibration standards employed in terms of their respective chemical and separation properties and in terms of their respective gas chromatographic and mass spectrometric responses. Using these assumptions, for example, the $^{13}C_{12}$-2,3,7,8-TCDD internal standard is utilized as the internal calibration standard for all of the 22 TCDD isomers or congeners. Furthermore, the concentration of the total TCDD present in a sample extract is determined by calculating, on the basis of the standard procedure outlined above, the concentration of each TCDD isomer peak (or peaks for multiple TCDD isomers, where these coelute) and these individual concentrations are subsequently summed to obtain the concentration of "total" TCDD.

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[c] In practice, the analyst can estimate the baseline noise by measuring the extension of the baseline immediately prior to each of the two mass chromatographic peaks attributed to a given PCDD or PCDF. Spurious signals may arise either from electronic noise or from other organic compounds in the extract. Since it may be desirable to evaluate the judgement of the analyst in this respect, copies of original mass chromatograms must be included in the report of analytical results.

8.6 Frequently, during the analysis of actual sample extracts, extraneous compounds which are present in the extract (those organic compounds not completely removed during the clean-up phase of the analysis) can cause changes in the liquid and gas chromatographic elution characteristics of the PCDD/PCDF (typically retention times for the PCDD/PCDF are prolonged). Such extraneous organic compounds, when introduced into the mass spectrometer source may also result in a decrease in the sensitivity of the MS because of suppression of ionization, and other affects such as charge transfer phenomena. The shifts in chromatographic retention times are usually general shifts, that is, the relative retention times for the PCDD/PCDF are not changed, although the entire elution time scale is prolonged. The analyst's intervention in the GC-MS operating sequence can correct for the lengthened GC retention times which are sometimes observed due to the presence of extraneous organics in the sample extract. For example, using the program outlined in Table 1, if the retention time observed for 2,3,7,8-TCDD (which normally is 19.5 minutes) is lengthened by 30 seconds or more, appropriate adjustments in the programming sequence outlined in Table 1 can be made, that is, each selected ion-monitoring program is delayed by a length of time proportionate to the lengthening of the retention time for the 2,3,7,8-TCDD isomer. In the case of ionization suppression, this phenomenon is inherently counteracted by the internal standard approach. However, if loss of sensitivity due to ionization suppression is severe, additional clean-up of the sample extract may be required in order to achieve the desired detection limits.

## 9. Quality Assurance/Quality Control

9.1 Quality assurance and quality control are ensured by the following provisions:

9.1.1 Each sample analyzed is spiked with stable isotopically labelled internal standards, prior to extraction and analysis. Recoveries obtained for each of these standards should typically be in the range from 60-90%. Since these compounds are used as true internal standards however, lower recoveries do not necessarily invalidate the analytical results for native PCDD/PCDF, but may result in higher detection limits than are desired.

9.1.2 Processing and analysis of at least one method blank sample is accomplished for each set of samples (a set being defined as 20 samples or less).

9.1.3 It is desirable to analyze at least one sample spiked with representative native PCDD/PCDF for each set of 20 or fewer samples. The result of this analysis provides an indication of the efficacy of the entire analytical procedure. The results of this analysis will be considered acceptable if the detected concentration of each of the native

PCDD/PCDF added to the sample is within ±50% of the known concentration. (An appropriate set of native isomers to be added here is a set such as that indicated for Standard Mixture C.)

9.1.4 At least one of the samples analyzed out of each set (of 20 samples or less) is analyzed in duplicate and the results of the duplicate analysis are included in the report of data.

9.1.5 Performance evaluation samples prepared by EPA, or other laboratories, which contain representative PCDD/PCDF in concentrations approximating those present in typical field samples being analyzed (but unknown to the analyzing lab) should be periodically distributed to laboratories accomplishing these analyses.

9.1.6 Sources of all calibration and performance standards used in the analyses and the purity of these materials must be specified in the data report.

## 10. Data Reporting

10.1 Each report of analyses accomplished using the protocol described herein will typically include tables of results which include the following:

10.1.1 Complete identification of the samples analyzed (sample numbers and source).

10.1.2 The dates and times at which all analyses were accomplished. This information should also appear on each mass chromatogram included with the report.

10.1.3 Raw mass chromatographic data which consists of the absolute intensities (based on either peak height or peak area) of the signals observed for the ion-masses monitored (See Table 1).

10.1.4 The calculated ratios of the intensities of the molecular ions for all PCDD/PCDF detected.

10.1.5 The calculated concentrations of native 2,3,7,8-TCDD and 2,3,7,8-TCDF, and the total concentrations of the congeners of each class of PCDD/PCDF for each sample analyzed, expressed in nanograms TCDD per gram of sample (that is, parts-per-billion) as determined from the raw data. If no PCDD/PCDF are detected, the notation "Not Detected" or "N.D." is used, and the minimum detectable concentrations

PCDD/PCDF added to the sample is within ±50% of the known concentration. (An appropriate set of native isomers to be added here is a set such as that indicated for Standard Mixture C.)

9.1.4 At least one of the samples analyzed out of each set (of 20 samples or less) is analyzed in duplicate and the results of the duplicate analysis are included in the report of data.

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10.1.4 The calculated ratios of the intensities of the molecular ions for all PCDD/PCDF detected.

10.1.5 The calculated concentrations of native 2,3,7,8-TCDD and 2,3,7,8-TCDF, and the total concentrations of the congeners of each class of PCDD/PCDF for each sample analyzed, expressed in nanograms TCDD per gram of sample (that is, parts-per-billion) as determined from the raw data. If no PCDD/PCDF are detected, the notation "Not Detected" or "N.D." is used, and the minimum detectable concentrations (or detection limits) are reported.

10.1.6 The same raw and calculated data which are provided for the actual samples will also be reported for the duplicate analyses, the method blank analyses, the spiked sample analyses and any other QA or performance samples analyzed in conjunction with the actual sample set(s).

10.1.7 The recoveries of the internal standards in percent.

10.1.8 The recoveries of the native PCDD/PCDF from spiked samples in percent.

10.1.9 The calibration data, including response factors calculated from the three point calibration procedure described elsewhere in this protocol. Data showing that these factors have been verified at least once during each 8 hour period of operation or with each separate set of samples analyzed must be included.

10.1.10 The weight or quantity of the original sample analyzed.

10.1.11 Documentation of the source of all PCDD/PCDF standards used and available specifications on purity.

10.1.12 In addition to the tables described above, each report of analyses will include all mass chromatograms obtained for all samples analyzed, as well as for all calibration, GC column performance, and GC "window" definition runs and results of column performance checks.

10.1.13 Any deviations from the procedures described in this protocal which are applied in the analyses of samples will be documented in detail in the analytical report.

## 11. Typical Data Indicative of Method Performance - Precision and Accuracy.

11.1 The method described herein has typically been employed to quantitatively determine 2,3,7,8-TCDD in combustion product samples at concentrations as low as 10 picograms/gram and as high at 100 μg/g. Concentrations of the other PCDD/PCDF which can be detected typically fall within the range of 20 picograms/isomer/gram of sample, to 100 picograms/g of sample. Of course, the limits of detection which can be practically achieved are dependent on the quantity of sample available and the amount and kind of other interferring organic residues which are present in the sample. With respect to precision, the average deviation of data obtained from the analyses of a number of aliquots of the same sample containing the 2,3,7,8-TCDD isomer in the 250-300 ppb range is estimated to be ±10% or better. Data on the precision of quantitation of multiple PCDD/PCDF in a single sample are not as yet available. As yet, there is inadequate interlaboratory and performance evaluation data available to specify the accuracy which can be expected of the analytical procedures described herein.

TABLE 1. Sequence of Operations in GC-MS-DS Quantitation of CDDs/CDFs in Extracts of Environmental Samples

| Elapsed Time (min) | Event | GC Column Temperature* (°C) | Temperature Program Rate (°C/min) | Ions Monitored by Mass Spectrometer (m/z) | Identity of Fragment Ion | Compounds Monitored | Approximate Theoretical Ratio of $[M]^+:[M+2]^+$ |
|---|---|---|---|---|---|---|---|
| 0.00 | Injection, splitless | 190 | | | | | |
| 1.00 | Turn on split valve | 190 | | | | | |
| 1.00 | Begin temp. program to 220°C | 190 | 5 | | | | |
| 6.00 | Open column flow to mass spectrometer | 215 | 5 | | | | |
| 7.00 | Column temperature hold | 220 | | | | | |
| 14.00 | Start Tetra Program; sweep = 350 ppm; time/mass = 0.08 sec. | | | 240.930 | $[M-COCl]^+$ | TCDF | |
| | | | | 258.930 | $[M-COCl]^+$ | TCDD | |
| | | | | 303.902 | $[M]^+$ | TCDF | 0.77 |
| | | | | 305.899 | $[M+2]^+$ | TCDF | |
| | | | | 315.942 | $[M]^+$ | $^{13}C_{12}$-TCDF | |
| | | | | 319.897 | $[M]^+$ | TCDD | 0.77 |
| | | | | 321.894 | $[M+2]^+$ | TCDD | |
| | | | | 327.885 | $[M]^+$ | $^{37}Cl_4$-TCDD | |
| | | | | 331.937 | $[M]^+$ | $^{13}C_{12}$-TCDD | |
| | | | | 373.840 | $[M]^+$ | HxDPE$^{a}$. | |
| 22.00 | Stop Tetra Program | 220 | | | | | |
| 22.60 | Start Penta Program; sweep = 350 ppm; time/mass = 0.12 sec. | | | 274.099 | $[M-COCl]^+$ | PeCDF | |
| | | | | 290.094 | $[M-COCl]^+$ | PeCDD | |
| | | | | 337.863 | $[M]^+$ | PeCDF | 0.61 |
| 23.00 | Begin temp. program to 235° | 220 | 5 | 339.860 | $[M+2]^+$ | PeCDF | |
| 26.00 | Column temperature hold | 235 | | 353.858 | $[M]^+$ | PeCDD | 0.61 |
| | | | | 355.855 | $[M+2]^+$ | PeCDD | |
| | | | | 407.801 | $[M]^+$ | HpDPE$^{a}$. | |
| 32.00 | Stop Penta Program | | | | | | |
| 32.60 | Start Hexa Program; sweep = 350 ppm; time/mass = 0.20 sec. | 235 | | 310.057 | $[M-COCl]^+$ | HxCDF | |
| | | | | 326.052 | $[M-COCl]^+$ | HxCDD | |
| | | | | 373.821 | $[M]^+$ | HxCDF | 1.23 |
| | | | | 375.821 | $[M+2]^+$ | HxCDF | |
| | | | | 385.861 | $[M]^+$ | $^{13}C_{12}$-HxCDF | |
| | | | | 389.816 | $[M]^+$ | HxCDD | 1.23 |
| | | | | 391.813 | $[M+2]^+$ | HxCDD | |
| | | | | 411.856 | $[M]^+$ | $^{13}C_{12}$-HxCDD | |
| | | | | 443.759 | $[M]^+$ | ODPE$^{a}$. | |

TABLE 1. Sequence of Operations in GC-MS-DS Quantitation of CDDs/CDFs in Extracts of Environmental Samples (Cont.)

| Elapsed Time (min) | Event | GC Column Temperature (°C) | Temperature Program Rate (°C/min) | Ions Monitored by Mass Spectrometer (m/z) | Identity of Fragment Ion | Compounds Monitored | Approximate Theoretical Ratio of [M]+:[M+2]+ |
|---|---|---|---|---|---|---|---|
| 33.00 | Begin temp. program to 250°C | 235 | 5 | | | | |
| 36.00 | Column temperature hold | 250 | | | | | |
| 42.50 | Stop Hexa Program | | | | | | |
| 43.00 | Start Hepta Program; sweep = 350 ppm; time/mass = 0.30 sec. | 250 | | 344.818 | $[M-COCl]^+$ | HpCDF | |
| | | | | 360.813 | $[M-COCl]^+$ | HpCDD | |
| | | | | 407.782 | $[M]^+$ | HpCDF | |
| | | | | 409.779 | $[M+2]^+$ | HpCDF | 1.03 |
| | | | | 423.777 | $[M]^+$ | HpCDD | |
| | | | | 425.774 | $[M+2]^+$ | HpCDD | 1.03 |
| 53.00 | Stop Hepta Program | 250 | | 477.720 | $[M^+]$ | NDPE$^a$. | |
| 53.50 | Start Octa Program; sweep = 350 ppm; time/mass = 0.30 sec. | 250 | | 378.768 | $[M-COCl]^+$ | OCDF | |
| | | | | 394.774 | $[M-COCl]^+$ | OCDD | |
| 54.00 | Begin temp. program to 270° | 250° | 5 | 441.732 | $[M]^+$ | OCDF | |
| 58.00 | Column temperature hold | 270° | | 443.780 | $[M+2]^+$ | OCDF | 0.88 |
| | | | | 453.772 | $[M]^+$ | $^{13}C_{12}$-OCDF | |
| | | | | 457.738 | $[M]^+$ | OCDD | |
| | | | | 459.735 | $[M+2]^+$ | OCDD | 0.88 |
| | | | | 469.779 | $[M]^+$ | $^{13}C_{12}$-OCDD | |
| | | | | 471.776 | $[M+2]^+$ | $^{13}C_{12}$-OCDD | |
| 65.00 | Stop Octa Program | | | 511.681 | $[M]^+$ | DDPE$^a$. | |
| 65.00 | Begin temp. program to 300° | 270° | 5 | | | | |
| 71.00 | Column temperature hold | 300° | | | | | |
| 75.00 | Cool Column to 190° | | | | | | |

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[a] HxDPE, HpDPE, ODPE, NDPE, DDPE are abbreviations which designate (respectively) hexachloro-, heptachloro-, octachloro-, nonachloro-, and decachlorodiphenyl ethers.

*The parameters given here are applicable for a 60-meter fused silica capillary GC column coated with DB-5.

# APPENDIX C

# ANALYTICAL METHODS FOR PCBs

# Method 680. Determination of Pesticides and PCBs in Water and Soil/Sediment by Gas Chromatography/Mass Spectrometry

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## 1. SCOPE AND APPLICATION

1.1. This method provides procedures for mass spectrometric determination of polychlorinated biphenyls (PCBs) and the listed pesticides in water, soil, or sediment. This method is applicable to samples containing PCBs as single congeners or as complex mixtures, such as commercial Aroclors. PCBs are identified and measured as isomer groups (i.e., by level of chlorination). The existence of 209 possible PCB congeners makes impractical the listing of the Chemical Abstracts Service Registry Number (CASRN) for each potential method analyte. Because PCBs are identified and measured as isomer groups, the non-specific CASRN for each level of chlorination is used to describe method analytes.

| Analyte(s) | Formula | CASRN |
|---|---|---|
| Aldrin | $C_{12}H_8Cl_6$ | 309-00-2 |
| BHCs | | |
| alpha isomer | $C_6H_6Cl_6$ | 319-84-6 |
| beta isomer | $C_6H_6Cl_6$ | 319-85-7 |
| delta isomer | $C_6H_6Cl_6$ | 319-86-8 |
| gamma isomer(lindane) | $C_6H_6Cl_6$ | 58-89-9 |
| Chlordane (technical) | | 57-74-9 |
| alpha-chlordane | $C_{10}H_6Cl_8$ | 5103-71-9 |
| gamma-chlordane | $C_{10}H_6Cl_8$ | 5103-74-2 |
| trans-nonachlor | $C_{10}H_5Cl_9$ | 39765-80-5 |
| 4,4'-DDD | $C_{14}H_{10}Cl_4$ | 72-54-8 |
| 4,4'-DDE | $C_{14}H_8Cl_4$ | 72-55-9 |
| 4,4'-DDT | $C_{14}H_9Cl_5$ | 50-29-3 |
| Dieldrin | $C_{12}H_8Cl_6O$ | 60-57-1 |
| Endosulfan I | $C_9H_6Cl_6O_3S$ | 959-98-8 |
| Endosulfan II | $C_9H_6Cl_6O_3S$ | 33213-65-9 |
| Endosulfan sulfate | $C_9H_4Cl_6O_4S$ | 1031-07-8 |
| Endrin | $C_{12}H_8Cl_6O$ | 72-20-8 |
| Endrin aldehyde | $C_{12}H_8Cl_6O$ | 7421-93-4 |
| Endrin ketone | $C_{12}H_8Cl_6O$ | 53494-70-5 |
| Heptachlor | $C_{10}H_5Cl_7$ | 76-44-8 |
| Heptachlor epoxide | $C_{10}H_5Cl_7O$ | 1024-57-3 |
| Methoxychlor | $C_{16}H_{15}Cl_3O_2$ | 72-43-5 |
| PCBs | | |
| Monochlorobiphenyls | $C_{12}H_9Cl$ | 27323-18-8 |
| Dichlorobiphenyls | $C_{12}H_8Cl_2$ | 25512-42-9 |
| Trichlorobiphenyls | $C_{12}H_7Cl_3$ | 25323-68-6 |
| Tetrachlorobiphenyls | $C_{12}H_6Cl_4$ | 26914-33-0 |
| Pentachlorobiphenyls | $C_{12}H_5Cl_5$ | 25429-29-2 |
| Hexachlorobiphenyls | $C_{12}H_4Cl_6$ | 26601-64-9 |
| Heptachlorobiphenyls | $C_{12}H_3Cl_7$ | 28655-71-2 |
| Octachlorobiphenyls | $C_{12}H_2Cl_8$ | 31472-83-0 |
| Nonachlorobiphenyls | $C_{12}HCl_9$ | 53742-07-7 |
| Decachlorobiphenyl | $C_{12}Cl_{10}$ | 2051-24-3 |

1.2 Detection limits vary among method analytes and with sample matrix, sample preparation procedures, condition of the GC/MS system, type of data acquisition, and individual samples. The calculated method detection limit (MDL) for each pesticide in fortified reagent water extracts analyzed with full-range data acquisition is presented in Sect. 14. Analysis of calibration solutions indicated that the calculated MDLs do not accurately reflect instrumental detection limits. The following guidance is based on numerous analyses of calibration solutions with one instrument over a period of approximately six months. Pesticide analytes other than endosulfans I and II can be identified and accurately measured when the injected aliquot contains 2 ng of each analyte; the endosulfans require about 4 ng each. With selected-ion-monitoring (SIM) data acquisition, pesticide analyte detection limits are lowered by at least a factor of five. Detection limits for individual PCB congeners increase with increasing number of chlorine atoms, with the detection limit for decachlorobiphenyl being about 5-10 times higher than that of a monochlorobiphenyl. A monochlorobiphenyl can be identified and accurately measured when the injected extract aliquot contains 1 ng and full-range data are acquired. The detection limit for total PCBs will depend on the number of individual PCB congeners present. SIM data acquisition procedures reduce the detection limit for PCBs by at least a factor of three.

## 2. SUMMARY OF METHOD

A 1-L water sample is placed in a separatory funnel and extracted with methylene chloride. Appropriate extraction procedures for soil/sediment samples will be added when results are obtained from ongoing experiments. The extract is dried and exchanged to hexane during concentration to a final volume of 1 mL or less. Sample extract components are separated with capillary column gas chromatography (GC) and identified and measured with low resolution, electron ionization mass spectrometry (MS). An interfaced data system (DS) to control data acquisition and to store, retrieve, and manipulate mass spectral data is essential. Either full-range or selected-ion-monitoring (SIM) data are acquired, depending on the concentration range of concern. If full-range data are acquired, all method analytes can be identified and measured with one GC/MS analysis. If all pesticides and PCBs must be determined and if SIM data are necessary to meet required detection limits, two GC/MS analyses are necessary, one to detect and measure pesticides and one to detect and measure PCBs.

Two surrogate compounds are added to each sample before sample preparation; these compounds are $^{13}C_{12}$-4,4'-DDT and $^{13}C_6$-gamma-BHC. Two internal standards, chrysene-$d_{12}$ and phenanthrene-$d_{10}$, are added to each sample extract before GC/MS analysis and are used to calibrate MS response. Each concentration measurement is based on an integrated ion abundance of one characteristic ion. All pesticides are identified as individual compounds, and a concentration is calculated by relating the MS response of each compound to the MS response of the internal standard with GC retention time nearer that of the pesticide analyte. The extent of sample contamination with technical chlordane is indicated by identification and measurement of the two most persistent components, gamma-chlordane and nonachlor. (Alpha-chlordane and heptachlor, other major components of technical chlordane, may also be present and will be detected and measured with this method.)

PCBs are identified and measured as isomer groups (i.e., by level of chlorination). A concentration is measured for each PCB isomer group; total PCB concentration in each sample extract is obtained by summing isomer group concentrations.

Nine selected PCB congeners are used as calibration standards, and one internal standard, chrysene-$d_{12}$, is used to calibrate MS response to PCBs, unless sample conditions require the use of the second internal standard, phenanthrene-$d_{10}$.

## 3. DEFINITIONS

3.1 CONCENTRATION CALIBRATION SOLUTION (CAL) -- A solution of method analytes used to calibrate the mass spectrometer response.

3.2 CONGENER NUMBER -- Throughout this method, individual PCBs are described with the number assigned by Ballschmiter and Zell (2). (This number is also used to describe PCB congeners in catalogs produced by Ultra Scientific, Hope, RI.)

3.3 INTERNAL STANDARD -- A pure compound added to a sample extract in known amounts and used to calibrate concentration measurements of other compounds that are sample components. The internal standard must be a compound that is not a sample component.

3.4 LABORATORY DUPLICATES (LD1 and LD2) --Two sample aliquots taken in the analytical laboratory are analyzed with identical procedures. Analysis of laboratory duplicates indicates precision associated with laboratory procedures but not with sample collection, preservation or storage procedures.

3.5 LABORATORY PERFORMANCE CHECK SOLUTION (LPC) -- A solution of method analytes, surrogate compounds, and internal standards used to evaluate the performance of the GC/MS/DS with respect to a defined set of method criteria.

3.6 LABORATORY REAGENT BLANK (LRB) -- An aliquot of reagent water or neutral solid reference material that is treated as a sample. It is exposed to all glassware and apparatus, and all method solvents, reagents, internal standards, and surrogate compounds are used. The extract is concentrated to the final volume used for samples and is analyzed the same as a sample extract.

3.7 LABORATORY SPIKE DUPLICATE SAMPLE -- One aliquot (LSD) of a sample is analyzed before fortification with any method analytes. In the laboratory, a known quantity of method analytes (LSA) is added to two independent aliquots of the same sample, and final analyte concentrations (LF1 and LF2) are measured with the same analytical procedures used to measure LSD.

3.8 LABORATORY SURROGATE SPIKE

3.8.1 Measured Value (LS1) -- Surrogate compound concentration measured with the same procedures used to measure sample components.

3.8.2 Theoretical Value (LS2) -- The concentration of surrogate compound added to a sample aliquot before extraction. This value is determined from standard gravimetric and volumetric techniques used during sample fortification.

3.9 METHOD DETECTION LIMIT (MDL) -- A statistically determined value (1) indicating the minimum concentration of an analyte that can be identified and measured in a sample matrix with 99% confidence that the analyte concentration is greater than zero. This value varies with the precision of the replicate measurements used for the calculation.

3.10 PERFORMANCE EVALUATION SAMPLE — A sample containing known concentrations of method analytes that has been analyzed by multiple laboratories to determine statistically the accuracy and precision that can be expected when a method is performed by a competent analyst. Analyte concentrations are unknown to the analyst.

3.11 QUALITY CONTROL (QC) CHECK SAMPLE — A sample containing known concentrations of analytes that is analyzed by a laboratory to demonstrate that it can obtain acceptable identifications and measurements with procedures to be used to analyze environmental samples containing the same or similar analytes. Analyte concentrations are known by the analyst. Preparation of the QC check sample by a laboratory other than the laboratory performing the analysis is highly desirable.

3.12 SURROGATE COMPOUND -- A compound not expected to be found in the sample is added to a sample aliquot before extraction and is measured with the same procedures used to measure sample components. Associated with the surrogate compound are two values, laboratory surrogate spike- measured value (LS1) and laboratory surrogate spike - theoretical value (LS2). The purpose of a surrogate compound is to monitor method performance with each sample.

## 4. INTERFERENCES

4.1 Interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing equipment. Laboratory reagent blanks (LRBs) are analyzed routinely to demonstrate that these materials are free of interferences under the analytical conditions used for samples.

4.2 To minimize interferences, glassware (including sample bottles) should be meticulously cleaned. As soon as possible after use, rinse glassware with the last solvent used. Then wash with detergent in hot water and rinse with tap water followed by distilled water. Drain dry and heat in a muffle furnace at 450°C for a few hours. After cooling, store glassware inverted or covered with aluminum foil. Before using, rinse each piece with an appropriate solvent. Volumetric glassware should not be heated in a muffle furnace.

4.3 For both pesticides and PCBs, interference can be caused by the presence of much greater quantities of other sample components that overload the capillary column; additional sample extract preparation procedures must then be used to eliminate interferences. Capillary column GC retention times and the compound-specific characteristics of mass spectra eliminate many interferences that formerly were of concern with pesticide/PCB determinations with electron capture detection. The approach and identification criteria used in this method for PCBs eliminate interference by most chlorinated compounds other than other PCBs. With the isomer group approach, coeluting PCBs that contain the same number of chlorines are identified and measured together. Therefore, coeluting PCBs are a problem only if they contain a different number of chlorine atoms. This interference problem is obviated by rigorous application of the identification criteria described in this method.

4.4 For SIM identification and measurement of pesticides, other chlorinated sample components that produce the same quantitation and confirmation ions may interfere, but only if retention times are nearly equivalent.

## 5. SAFETY

5.1 The toxicity or carcinogenicity of each chemical used in this method has not been precisely defined. Therefore, each should be treated as a potential health hazard, and exposure should be reduced to the lowest feasible level. Each laboratory is responsible for safely disposing materials and for maintaining awareness of OSHA regulations regarding safe handling of the chemicals used in this method. A reference file of material data handling sheets should be made available to all personnel involved in analyses. Additional information on laboratory safety is available (3-5).

5.2 The following method analytes have been classified as known or suspected human or mammalian carcinogens: BHCs, 4,4'-DDD, 4,4'-DDT, and PCBs. Primary standards of these compounds should be prepared in a hood. A toxic gas respirator should be worn when the analyst handles solutions containing high concentrations of these compounds.

## 6. APPARATUS AND EQUIPMENT

### 6.1 SAMPLING EQUIPMENT

6.1.1 Water Sample Bottles -- Meticulously cleaned (Sect. 4.2) 1-L or 1-qt amber glass fitted with a Teflon-lined screw cap. (Bottles in which high purity solvents were received can be used as sample bottles without additional cleaning if they have been handled carefully to avoid contamination during and after use of original contents.)

6.1.2 Soil/Sediment Sample Bottles -- Appropriate containers will be specified when appropriate extraction procedures are determined.

### 6.2 GLASSWARE

6.2.1 Separatory Funnel -- 2-L with Teflon stopcock.

6.2.2 Drying Column -- glass column approximately 400 mm long X 19 mm ID with coarse frit filter disc.

6.2.3 Chromatography Column -- glass column approximately 400 mm long X 19 mm ID with coarse frit filter disc and Teflon stopcock.

6.2.4 Concentrator Tube -- 10-mL graduated Kuderna-Danish design with ground-glass stopper.

6.2.5 Evaporative Flask -- 500-mL Kuderna-Danish design that is attached to concentrator tube with springs.

6.2.6 Snyder Column -- three-ball macro Kuderna-Danish design.

6.2.7 Vials -- 10- to 15-mL amber glass with Teflon-lined screw caps.

## 6.3 COMPUTERIZED GC/MS SYSTEM

6.3.1 The GC must be capable of temperature programming and be equipped with all required accessories, such as syringes, gases, and a capillary column. The GC injection port must be designed for capillary columns. Manual splitless injections were used to acquire data used as the basis for quality control requirements. An automatic injector, however, is desirable, because it should provide more precise retention times and areas. On-column injection with an uncoated precolumn is encouraged, because high mass descrimination and analyte degradation problems are minimized with this technique. With some GCs, however, the irreproducibility of the low initial column temperature required for on-column injections will cause irreproducible retention times (RTs) and relative retention times (RRTs). That can result in an inability to distinguish between two closely-eluting pesticide isomers and may cause ion sets to be changed at inappropriate times during SIM data acquistion. Splitting injections are not recommended.

6.3.2 Either full range or SIM mass spectral data are obtained with electron ionization at a nominal electron energy of 70 eV. To ensure sufficient precision of mass spectral data, the required MS scan rate must allow acquisition of at least five full-range mass spectra or five data points for each monitored ion while a sample component elutes from the GC. The MS must produce a mass spectrum meeting all criteria for $\leq$20 ng of decafluorotriphenylphosphine (DFTPP) introduced through the GC inlet.

6.3.3 An interfaced data system (DS) is required to acquire, store, reduce, and output mass spectral data. The DS must be capable of searching a data file for specific ions and plotting ion abundances versus time or spectrum number to produce selected ion current profiles (SICPs) and extracted ion current profiles (EICPs). Also required is the capability to obtain chromatographic peak areas between specified times or spectrum numbers in SICPs or EICPs. Total data acquisition time per cycle should be $\geq$0.5 s and must not exceed 1.5 s.

6.3.4 SIM Option -- For SIM data acquisition, the DS must be equipped with software capable of acquiring data for multiple groups of ions, and the DS must allow automated and rapid changes of the set of ions being monitored. To acquire all PCB data needed for implementation of two currently-available automated interpretation procedures, the SIM program must be capable of acquiring data for four groups (or mass ranges) each consisting of $\leq$35 ions or for five groups of $\leq$20 ions each. The times spent monitoring ions during sample analyses must be the same as the times used when calibration solutions were analyzed.

6.4 GC COLUMN — A 30 m X 0.32 mm ID fused silica capillary column coated with a 0.25 um or thicker film crosslinked phenyl methyl silicone (such as Durabond-5 (DB-5), J and W Scientific, Rancho Cordova, CA) or polydiphenyl vinyl dimethyl siloxane (such as SE-54, Alltech Associates, Deerfield, IL) is required. Operating conditions known to produce acceptable results with these columns are shown in Table 1; separation of pesticide analytes and PCB calibration congeners with a DB-5 column and those operating conditions is shown in Figure 1. Retention times have been reported (6) for all 209 PCB congeners with an SE-54 column, which provides the same retention order for PCBs and essentially the same separation capabilities as a DB-5 column.

### 6.5 MISCELLANEOUS EQUIPMENT

6.5.1 Volumetric flasks - 2-mL, 5-mL, 10-mL, 25-mL, and 50-mL with ground glass stoppers.

6.5.2 Microsyringes - various standard sizes.

6.5.3 Boiling Chips -- approximately 10/40 mesh. Heat at 400°C for 30 min or extract with methylene chloride in a Soxhlet apparatus.

6.5.4 Water Bath -- heated, with concentric ring cover, capable of temperature control within ± 2°C.

6.5.5 Analytical Balance -- capable of accurately weighing to 0.0001 g.

## 7. REAGENTS AND CONSUMABLE MATERIALS

7.1 SOLVENTS — High purity, distilled-in-glass hexane and methylene chloride. For precise injections with splitless injectors and capillary columns, all samples and standards should be contained in the same solvent. Effects of minor variations in solvent composition (i.e., small percentage of another solvent remaining in hexane extracts) are minimized with the use of internal standards. (External standard calibration is not acceptable.)

7.2 SODIUM SULFATE — ACS, granular, anhydrous. Purify by heating at 400°C for 4 h in a shallow tray.

7.3 SODIUM THIOSULFATE — ACS, granular.

7.4 TETRABUTYLAMMONIUM SULFITE REAGENT — Dissove 3.39 g of tetrabutylammonium hydrogen sulfate in 100 mL distilled water. To remove impurities extract solution three times with 20-mL portions of hexane. Discard the hexane extracts, and add 25 g sodium sulfite to the water solution. Store the resulting solution in an amber bottle with a Teflon-lined screw cap. The solution can be stored at room temperature for at least one month.

7.5. MS PERFORMANCE CHECK SOLUTION — Prepare a 10 ng/uL solution of decafluorotriphenylphosphine (DFTPP) in an appropriate solvent.

7.6 INTERNAL STANDARDS — Chrysene-$d_{12}$ and phenanthrene-$d_{10}$ are used as internal standards. They are added to each sample extract just before analysis and are contained in all calibration/performance check solutions.

7.7 SURROGATE COMPOUNDS — $^{13}C_{12}$-4,4'-DDT and $^{13}C_{6}$-gamma-BHC are added to every sample before extraction and are included in every calibration/performance check solution.

7.8 PCB CONCENTRATION CALIBRATION CONGENERS — The nine individual PCB congeners listed in Table 2 are used as concentration calibration compounds for PCB determinations. One isomer at each level of chlorination is used as the concentration calibration standard for all other isomers at that level of chlorination, except that decachlorobiphenyl ($Cl_{10}$) is used for both $Cl_9$

and $Cl_{10}$ isomer groups. The basis for selection of these calibration congeners has been reported (7).

7.9 PCB RETENTION TIME CONGENERS FOR SIM DATA ACQUISITION OPTION -- Knowledge of the retention times of certain congeners is necessary to determine when to acquire data with each ion set. Two concentration calibration congeners also serve as retention time congeners; the first eluting $Cl_1$-PCB indicates the time when data acquisition must have been initiated for ion set #1, and the $Cl_{10}$-PCB indicates when all PCBs have eluted. Two or three additional PCB congeners are used to establish times to initiate data acquisition with other ion sets (Sect. 9.4).

### 7.10 PESTICIDE SOLUTIONS

7.10.1 Pesticide Stock Solutions -- Prepare from pure standard materials. Weigh approximately 25.0 mg (with accuracy of 0.1 mg) of each surrogate compound and each pure pesticide analyte, except Endosulfan I and Endosulfan II. For those two pesticides, prepare a stock solution twice as concentrated as that prepared for other pesticide analytes. Dissolve each compound in hexane and dilute to volume in a 10-mL (5-mL for the two Endosulfans) volumetric flask. (Concentration of each component = 2.5 mg/mL, except Endosulfans, which should be 5 mg/mL.) Smaller or larger volumes of stock solution may be used if desired. If compound purity is certified at $\geq$96%, the weight can be used without correction to calculate the concentration of the stock standard solution. Commercially prepared stock standards in hexane can be used at any concentration if they are traceable to USEPA-supplied standards.

7.10.2 Pesticide Primary Dilution Solutions -- A convenient approach to solution preparation is to prepare two pesticide primary dilution solutions that are twice the concentration of the highest concentration calibration solution required. These solutions can then be diluted as necessary to prepare all needed calibration solutions. One solution contains endrin aldehyde and one does not, because the medium level calibration solution does not contain endrin aldehyde. Place 1 mL of each pesticide analyte/surrogate compound stock solution in a 25-mL volumetric flask. (Total volume for all 22 pesticide analytes and 2 surrogate compounds = 24 mL.) Make to volume with hexane and mix well. (Concentration of endosulfan sufate, endosulfan I and endosulfan II = 200 ng/uL; concentration of each other component = 100 ng/uL.)

### 7.11 PCB SOLUTIONS

7.11.1 Stock Solutions of PCB Calibration Congeners -- Prepare a stock solution of each of the nine PCB concentration calibration congeners at a concentration of 1 ug/uL in hexane. (If SIM data are to be acquired, prepare a 1 ug/uL stock solution of each of the three retention time congeners also.) Place each solution in a clean glass vial with a Teflon-lined screw cap and store at 4°C if solutions are not to be used right away. Solutions are stable indefinitely if solvent evaporation is prevented.
CAUTION: Each time a vial containing small volumes of solutions is warmed to room temperature and opened, a small volume of solvent in the vial headspace evaporates, significantly affecting concentration.

Solutions should be stored with the smallest possible volume of headspace, and opening vials should be minimized.

7.11.2 PCB Primary Dilution Standard — Take aliquots of the stock solutions of the nine PCB concentration calibration congeners and mix together in the proportions of one part of each solution of the $Cl_1$ (#1), $Cl_2$ (#5), and $Cl_3$ (#29) congeners, two parts of each solution of the $Cl_4$ (#50), $Cl_5$ (#87), and $Cl_6$ (#154) congeners, three parts of each solution of the $Cl_7$ (#188) and $Cl_8$ (#200) congeners, and five parts of the $Cl_{10}$ (#209) congener solution. (Note: The retention time congeners described in Sect. 7.9 are not included in the PCB primary dilution standard because they are not needed for full-range data acquisition.) This will provide a primary dilution standard solution of the composition shown in Table 3. Calculate the concentration in ug/uL; use three significant figures. Place each solution in a clean glass vial with a Teflon-lined screw cap and store at 4°C. Mark the meniscus on the vial wall to monitor solution volume during storage; solutions are stable indefinitely if solvent evaporation is prevented.

7.12 INTERNAL STANDARD (IS) SOLUTIONS — Two solutions are needed to prepare concentration calibration solutions (CALs).

7.12.1 IS solution #1 (for full-range CALS) -- Weigh 7.5 mg ± 0.1 mg each of phenanthrene-$d_{10}$ and chrysene-$d_{12}$; dissolve in hexane and dilute to 10 mL in a volumetric flask. (Concentration of each IS = 750 ng/uL)

7.12.2 IS solution #2 (for SIM CALS) -- Take 1 mL of IS solution #1 and dilute to 10 mL in a volumetric flask. (Concentration of each IS = 75 ng/uL)

7.13 CALS FOR FULL-RANGE DATA ACQUISITION — Five hexane solutions are required. The solutions contain constant concentrations of the ISs (chrysene-$d_{12}$ and phenanthrene-$d_{12}$) and varying concentrations of individual pesticide analytes, the nine PCB calibration compounds, and the two surrogate compounds ($^{13}C_{12}$-4,4'-DDT and $^{13}C_6$-gamma-BHC). (Composition and approximate concentrations are given in Table 4.) Four solutions (high and low concentrations) contain both ISs, both surrogate compounds, the nine PCB concentration calibration congeners, and each of the single-compound pesticide analytes. The fifth solution, the medium level concentration solution, contains all the above compounds except endrin aldehyde, which is not present for reasons described in Sect. 8. The lowest concentration solution contains each individual pesticide analyte and each PCB calibration congener at a concentration near but greater than its anticipated detection limit. (Because MS response to PCBs decreases with increasing level of chlorination, PCB congener concentrations in CALs increase with level of chlorination.) Components of the highest concentration solution (High CAL) are present at a concentration that allow injections of 2-uL aliquots without MS saturation or GC column overloading.

7.13.1 The Full-Range High CAL can be prepared by mixing equal portions of the PCB primary dilution solution and the pesticide primary dilution solution that contains endrin aldehyde and then adding an appropriate volume of IS solution #1. For example, 1 mL of each primary dilution solution and 20 uL of IS solution #1 provide the appropriate concentration for High CAL.

7.13.2 Other full-range CALS are prepared by diluting the primary dilution standard solutions and adding the appropriate amount of IS solution #1. CAUTION: The pesticide primary dilution standard that does not contain endrin aldehyde must be used for the medium level full-range CAL.

7.14 CALS FOR SIM DATA ACQUISITION OPTION — Two sets of solutions are needed, one set of five solutions for determinations of pesticide analytes, and one set of five solutions for PCB determinations. Appropriate concentrations of SIM CALs are given in Tables 5a and 5b. Solutions are prepared by diluting appropriate primary dilution standards and adding an appropriate volume of IS solution #2.
CAUTION: The Pesticide SIM Medium CAL does not contain endrin aldehyde; the PCB SIM CALS must include the three PCB retention time congeners. that are used to establish conditions for SIM data acquisition.

7.15 Prepare a solution of surrogate compounds in a water miscible solvent to provide a concentration in the sample/blank extract that is near the concentration anticipated for analytes when an aliquot of $\geq$20 uL is added to the sample before extraction.

7.15 Calculate the concentration (two significant figures if <100 and three significant figures if $\geq$100 ng/uL) of each component in each solution. Note: Concentrations presented in tables are only approximate.

7.16 LABORATORY PERFORMANCE CHECK SOLUTION - For both full-range data acquisition, and the SIM data acquisition option, the Medium CAL is used as the laboratory performance check solution (LPC) to verify response factors and to demonstrate adequate GC resolution and MS performance.

## 8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

### 8.1 WATER SAMPLES

8.1.1 Samples must be collected in clean (Sect. 4.2) glass containers. Note: When samples are anticipated to contain low concentrations of method analytes, a sample larger than 1-L may be needed. An effective sample collection procedure to minimize losses of hydrophobic analytes is to add a portion of extracting solvent to each sample container when the sample is collected. When a 1-gal sample is collected, an appropriate solvent volume is approximately 100 mL. (The entire sample must be used as one sample aliquot, and blank sample/solvent volumes must be adjusted also.)

8.1.2 Samples must be iced or refrigerated at 4°C from time of collection until extraction. If samples will not be extracted within 72 h after collection, use either sodium hydroxide or sulfuric acid to adjust sample pH to within a range of 5 to 9. Record the volume of acid or base used. If aldrin is to be determined, add sodium thiosulfate when residual chlorine is present. Field test kits are available for measurement of residual chlorine.

8.1.3 Samples should be extracted within 7 days after collection and analyzed within 40 days after extraction.

8.2 SOIL/SEDIMENT SAMPLES — Appropriate procedures will be specified when results are obtained from ongoing experiments.

## 9. CALIBRATION

Demonstration and documentation of acceptable initial calibration is required before any samples are analyzed and is required intermittently throughout sample analyses as dictated by results of continuing calibration checks. After initial calibration is successfully performed, a continuing calibration check is required at the beginning and end of each 12-h period during which analyses are performed. The Medium CALs for pesticide determinations do not include endrin aldehyde. This allows the Medium CAL to be used for continuing calibration checks, including a check to ensure that endrin decomposition is $\leq$10%. During initial calibration a separate Medium CAL containing endrin aldehyde and the internal standard is analyzed to determine the response factor for endrin aldehyde. Thereafter, if endrin aldehyde is a component of any sample and endrin decomposition is not a problem, the response factor for endrin aldehyde is verified by analyzing a calibration solution containing it.

9.1 DATA ACQUISITION OPTIONS — Either full-range or SIM data acquisition may be used.

9.1.1 Full-range data acquisition is recommended if sample extract components are anticipated to be at sufficiently high concentrations.

9.1.2 SIM data acquisition will provide an increase in sensitivity by at least a factor of five for pesticide determinations and by at least a factor of three for PCB determinations.

9.2. INITIAL CALIBRATION

9.2.1 Calibrate and tune the MS with standards and procedures prescribed by the manufacturer with any necessary modifications to meet USEPA requirements.

9.2.2 Inject a 1- uL or 2-uL aliquot of the 10 ng/uL DFTPP solution and acquire a mass spectrum that includes data for m/z 45-450. If the spectrum does not meet all criteria (Table 6), the MS must be hardware tuned to meet all criteria before proceeding with calibration.

9.2.3 Full-Range Calibration — Inject a 1- or 2-uL aliquot of the Medium CAL and acquire data from m/z 45 to 510. Acquire $\geq$5 spectra during elution of each GC peak. Total cycle time should be $\geq$0.5 s and $\leq$1.5 s. Note: Either a 1- or 2-uL aliquot should be used consistently for CALs and sample/blank extracts.

9.2.4 SIM Calibration — Acquire at least five data points for each ion during elution of each GC peak. Total cycle time should be $\geq$0.5 s and $\leq$1.5 s.
CAUTION: When acquiring SIM data, GC operating conditions must be carefully reproduced for each analysis to provide reproducible retention times; if not, ions will not be monitored at the appropriate times.

### 9.2.4.1 SIM Calibration for PCB determinations

9.2.4.1.1 Two options for SIM data acquisition are provided. Data can be acquired with four sets of ≤six mass ranges (≤35 ions each as shown in Table 7a) or with the five ion sets (≤20 ions each) shown in Tables 7b and 7c.

9.2.4.1.2 The time (scan number) for initiation of data acquisition with each ion set must be carefully determined from the retention times (scan numbers) of the retention time congeners. Approximate relative retention times of calibration congeners and approximate relative retention time windows for PCB isomer groups are shown in Table 8. (Also see Figures 1 and 2.)

9.2.4.1.3 SIM data acquisition with four ion sets. Begin data acquisition with Ion Set #1 before elution of PCB congener #1, the first eluting $Cl_1$-PCB. Stop acquisition with Ion Set #1 and begin acquisition with Ion Set #2 just (approximately 10 s) before elution of PCB congener #104, the first eluting $Cl_5$-PCB. Stop acquisition with Ion Set #2 and begin acquisition with Ion Set #3 just (approximately 10 s) after elution of PCB congener #77, the last eluting $Cl_4$-PCB. Stop acquisition with Ion Set #3 and begin acquisition with Ion Set #4 just (approximately 10 s) after elution of $^{13}C_{12}$-4,4'-DDT.

9.2.4.1.4 SIM data acquisition with five ion sets. Acquire data with the four Ion Sets described in Sect. 9.2.4.1.3 and add a fifth Ion Set beginning data acquisition with that set just (approximately 10 s) before elution of PCB congener #208, the first eluting $Cl_9$-PCB.

9.2.4.2 SIM Calibration for Pesticide Determinations -- Three sets of ≤15 ions each are used (Tables 9-10). Begin data acquisition with Ion Set #1 before elution of alpha-BHC, the first eluting pesticide analyte. Begin data acquisition with Ion Set #2 after elution of aldrin and before elution of heptachlor epoxide. Stop acquisition with Ion Set #2 and begin acquisition with Ion Set #3 after elution of endosulfan II and before 4,4'-DDD.

### 9.2.5 Performance Criteria

### 9.2.5.1 Full-Range Data from Analysis of Medium CAL

9.2.5.1.1 GC performance — baseline separation of beta-BHC and gamma-BHC; baseline separation of endrin ketone and chrysene-$d_{12}$; height of $Cl_1$-PCB peak ≥80% beta-BHC peak height; height of chrysene-$d_{12}$ peak ≥60% of the peak height of methoxychlor, which may partially coelute with the $Cl_8$-PCB congener.

9.2.5.1.2 MS sensitivity — Signal/noise ratio of ≥5 for m/z 499 of PCB congener #209, $Cl_{10}$-PCB.

9.2.5.1.3 MS calibration — Abundance of $\geq$40% and $\leq$60% of m/z 502 relative to m/z 498 for PCB congener #209.

9.2.5.1.4 Lack of degradation of endrin. Examine an extracted ion current profile (EICP) for m/z 67 in the retention time window between 4,4'-DDE and endosulfan sulfate; confirm that the abundance of m/z 67 at the retention time of endrin aldehyde is <10% of the abundance of m/z 67 produced by endrin.

9.2.5.1.5 Lack of degradation of $^{13}C_{12}$-4,4'-DDT. Examine EICPs for m/z 258 and m/z 247 in the retention time window that includes 4,4'-DDD, 4,4'-DDE and 4,4'-DDT; m/z 258 would be produced by $^{13}C_{12}$-4,4'DDE, and m/z 247 by $^{13}C_{12}$-4,4'-DDD. Confirm that the total abundance of both ions is <5% of m/z 247 produced by $^{13}C_{12}$-4,4'-DDT.

9.2.5.2 SIM PCB Data

9.2.5.2.1 GC separation — Baseline separation of PCB congener #87 from congeners #154 and #77, which may coelute.

9.2.5.2.2 MS sensitivity — Signal/noise ratio of $\geq$5 for m/z 499 of PCB congener #209, $Cl_{10}$-PCB, and for m/z 241 of chrysene-$d_{12}$.

9.2.5.2.3 MS calibration — Abundance of $\geq$70% and $\leq$95% of m/z 500 relative to m/z 498 for congener #209, $Cl_{10}$-PCB.

9.2.5.3 SIM Pesticide Data

9.2.5.3.1 GC separation — Baseline separation of endrin ketone and chrysene-$d_{12}$; baseline separation of beta-BHC and gamma-BHC; baseline separation of endrin ketone and chrysene-$d_{12}$; height of chrysene-$d_{12}$ peak $\geq$60% of methoxychlor peak height.

9.2.5.3.2 MS sensitivity — Signal/noise ratio of >5 for m/z 241 of chrysene-$d_{12}$.

9.2.5.3.3 MS calibration — Abundance of m/z 241 relative to that of m/z 240 produced by chrysene-$d_{12}$ is >15% and <25%.

9.2.5.3.4 Lack of degradation of endrin. Examine an SICP for m/z 67 in the retention time window between 4,4'-DDE and endosulfan sulfate; confirm that the abundance of m/z 67 at the retention time of endrin aldehyde is <10% that of m/z 67 produced by endrin.

9.2.5.3.5 Lack of degradation of $^{13}C_{12}$-4,4'-DDT. Examine SICPs for m/z 258 and m/z 247 in the retention time window that includes 4,4'-DDD, 4,4'-DDE, and 4,4'-DDT; m/z 258 would be produced by $^{13}C_{12}$-4,4'-DDE, and m/z 247 by $^{13}C_{12}$-4,4'-DDD. Confirm that the total abundance of both ions is <5% of m/z 247 produced by $^{13}C_{12}$-4,4'-DDT.

9.2.6 Replicate Analyses of CALs — If all performance criteria are met, analyze one 1- or 2-uL aliquot of each of the other four CALs.

9.2.7 Response Factor Calculation

9.2.7.1 Calculate five response factors (RFs) for each pesticide analyte, PCB calibration congener, and surrogate compound relative to both ISs (See Sect. 12.3.2), phenanthrene-$d_{10}$ and chrysene-$d_{12}$:

$$RF = A_x Q_{is} / A_{is} Q_x$$

where $A_x$ = integrated ion abundance of quantitation ion for a pesticide, a PCB calibration congener or a surrogate compound,

$A_{is}$ = integrated ion abundance of m/z 240, the quantitation ion when chrysene-$d_{12}$ is used as the internal standard or m/z 188, the quantitation ion when phenanthrene-$d_{10}$ is used as the internal standard,

$Q_{is}$ = injected quantity of chrysene-$d_{12}$ or phenanthrene-$d_{10}$,

$Q_x$ = injected quantity of pesticide analyte, PCB calibration congener or surrogate compound.

RF is a unitless number, units used to express quantities must be equivalent. Note: The $Cl_2$-PCB calibration congener may not be resolved from alpha-BHC. If not, alpha-BHC will contribute to the ion abundance measured for $Cl_2$-PCB. To correct for this contribution, subtract 6.7% of the ion abundance of m/z 219 measured for alpha-BHC from the ion abundance measured for m/z 222 for $Cl_2$-PCB.

9.2.8 Response Factor Reproducibility — For each pesticide analyte, PCB calibration congener and surrogate compound, calculate the mean RF from analyses of each of the five CALS. When the RSD exceeds 20%, analyze additional aliquots of appropriate CALS to obtain an acceptable RSD of RFs over the entire concentration range, or take action to improve GC/MS performance.

9.2.9 SIM Analyte Retention Time Reproducibility

9.2.9.1 PCB determinations - Absolute retention times of PCB congeners #77 and #104 should not vary by more than ±10 s from one analysis to the next. (Retention time reproducibility is not as critical for congeners #1 and #209 as for #77 and #104, which are used to determine when ion sets are changed.)

9.2.9.2 Pesticide determinations — Absolute retention times of gamma-chlordane, endosulfan I, and endosulfan II should not vary by more than ±10 s from one analysis to the next.

9.2.10 Record a spectrum of each CAL component.

## 9.3. CONTINUING CALIBRATION CHECK

9.3.1 With the following procedures, verify initial calibration at the beginning and end of each 12-h period during which analyses are to be performed.

9.3.2 Calibrate and tune the MS with standards and procedures prescribed by the manufacturer.

9.3.3 Analyze a 1-uL or 2-uL aliquot of the DFTPP solution and ensure acceptable MS calibration and performance (Table 6).

9.3.4 Inject a 1-uL or 2-uL aliquot of the Medium CAL and analyze with the same conditions used during Initial Calibration.

9.3.5 Demonstrate acceptable performance for criteria described in Sect. 9.2.5.

9.3.6 Determine that neither the area measured for m/z 240 for chrysene-$d_{12}$ nor that for m/z 188 for phenanthrene-$d_{10}$ has decreased by more than 30% from the area measured in the most recent previous analysis of a calibration solution or by more than 50% from the mean area measured during initial calibration.

9.3.7 Response Factor Reproducibility — For an acceptable Continuing Calibration Check, the measured RF for each analyte/surrogate compound must be within ±20% of the mean value calculated (Sect. 9.2.7) during Initial Calibration. If not, remedial action must be taken; recalibration may be necessary.

9.3.8 SIM Analyte Retention Time Reproducibility — Demonstrate and document acceptable (Sect. 9.2.9) reproducibility of absolute retention times of appropriate pesticide analytes and PCB retention time congeners.

9.3.9 Remedial actions must be taken if criteria are not met; possible remedies are:

9.3.9.1 Check and adjust GC and/or MS operating conditions.

9.3.9.2 Clean or replace injector liner.

9.3.9.3 Flush column with solvent according to manufacturers instructions.

9.3.9.4 Break off a short portion (approximately 0.33 m) of the column; check column performance by analysis of performance check solution.

9.3.9.5 Replace GC column; performance of all initial calibration procedures then required.

9.3.9.6 Adjust MS for greater or lesser resolution.

9.3.9.7 Calibrate MS mass scale.

9.3.9.8 Prepare and analyze new concentration calibration/performance check solution.

9.3.9.9 Prepare new concentration calibration curve(s).

## 10. QUALITY CONTROL

10.1 LABORATORY REAGENT BLANK (LRB) -- Perform all steps in the analytical procedure (Section 11) using all reagents, standards, surrogate compounds, equipment, apparatus, glassware, and solvents that would be used for a sample analysis; but omit an aliquot of sample (water or soil/sediment). For water samples, substitute 1 L of reagent water. If available, substitute EPA-provided reagent blank solid material for an aliquot of soil/sediment.

10.1.1 An LRB must contain the same amount of surrogate compounds and internal standards that is added to each sample. This amount will vary with sample type and with the type of data acquisition (full-range or SIM).

10.1.2 Analyze an LRB before any samples are extracted and analyzed.

10.1.3 Before a new batch of solvents or reagents is used for sample extraction or for column chromatographic procedures, analyze an LRB. In addition, analyze a laboratory solvent blank (LSB), which is the same as an LRB except that no surrogate compounds or internal standards are added; this demonstrates that reagents contain no impurities producing an ion current above the level of background noise for quantitation ions for those compounds.

10.1.4 Analyze an LRB along with each batch of $\leq$20 samples.

10.1.5 An acceptable LRB contains no method analyte at a concentration greater than one half of its MDL and contains no additional compounds with elution characteristics and mass spectral features that would interfere with identification and measurement of a method analyte at its MDL. If the LRB that was extracted along with a batch of samples is contaminated, the entire batch of samples must be reextracted and reanalyzed.

10.1.6 Corrective action for unacceptable LRB -- Check solvents, reagents, apparatus and glassware to locate and eliminate the source of contamination before any samples are extracted and analyzed. Purify or discard contaminated reagents and solvents.

10.2 CALIBRATION -- Included among initial and continuing calibration procedures are numerous quality control checks to ensure that valid data are acquired (See Sect. 9). Continuing calibration checks are accomplished with results from analysis of one solution, the medium level calibration solution for the appropriate type of data acquisition, either full-range or SIM.

10.2.1 If some criteria are not met for a Continuing Calibration Check after a 12-h period during which samples were analyzed, those samples must be reanalyzed. Those criteria are: GC performance (Sect. 9.2.5), MS calibration as indicated by DFTPP spectrum, and MS sensitivity as indicated by area of internal standards.

10.2.2 When other criteria in Sect. 9.2 are not met, results for affected analytes must be labeled as suspect to alert the data user of the observed problem. Included among those criteria are: response factor check for each analyte or PCB calibration congener, degradation of DDT and endrin, and retention time reproducibility for SIM data acquisition.

10.3 INITIAL DEMONSTRATION OF LABORATORY CAPABILITY FOR WATER ANALYSES (Insufficient information is currently available for demonstration for soil/ sediment analyses.)

10.3.1 Until appropriate Quality Control Check Samples are available, each laboratory should prepare one or more solutions containing each method analyte at a concentration corresponding to that anticipated in samples. Until accuracy and precision limits have been established for PCB isomer groups in appropriate samples, a solution containing an Aroclor mixture may be used; compare total measured PCB concentration to the total Aroclor concentration. Report Aroclor concentration and measured concentrations of PCB isomer groups and total measured PCB concentration.

10.3.2 Add an appropriate volume of a solution of method analytes to each of four 1-L aliquots of reagent water. Extract and analyze according to procedures in Sect. 11.

10.3.2 For each analyte, calculate measured concentrations, relative standard deviation of the four measurements, and method bias (Sect. 12.6).

10.4 LABORATORY PERFORMANCE CHECK SOLUTION — In this method, the medium level concentration calibration solution also serves the purpose of a laboratory performance check solution.

10.5 LABORATORY SURROGATE SPIKE

10.5.1 Measure the concentration of both surrogate compounds in every sample and blank.

10.5.2 Until performance based acceptance limits have been established for surrogate compounds, the following guidelines are provided: measured bias with LRB = -30% to +10%; measured bias with water or soil/sediment extract = -50% to +25%.

10.6 QUALITY CONTROL CHECK SAMPLE — Not yet available; anticipate need for analysis of one for each batch of ≤20 samples. If full-range data are acquired, both pesticide and PCB analytes can be determined with one analysis. If SIM data are acquired, one extraction and two GC/MS analyses will be needed to determine both PCBs and pesticides.

10.7 LABORATORY SPIKED DUPLICATE SAMPLE — Select one sample from each batch of ≤20 samples of similar type and fortify (spike) two aliquots of that sample with a solution containing appropriate concentrations of pesticide analytes and at least one Aroclor mixture. After addition of surrogate compounds, extract and analyze (Sect. 11) these two fortified aliquots along with an additional unfortified sample aliquot. Relative difference (RD) of duplicate results for surrogate compound concentrations should be ≤40%.

($RD = [C_1 - C_2 / 0.5 (C_1 + C_2)] 100$ ) Calculate bias (Sect. 12.6) for each analyte and surrogate compound. Insufficient data are currently available to provide guidance for acceptable bias and RD of measured analyte concentrations.

10.8 PERFORMANCE EVALUATION SAMPLE — Not yet available; to be analyzed periodically when available.

## 11. PROCEDURES

### 11.1 SAMPLE EXTRACTION

#### 11.1.1 Water Samples

11.1.1.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour entire sample into a 2-L separatory funnel. (If a sample larger than 1-L or 1-qt is extracted, the funnel size and solvent volume for samples and blanks must be adjusted also.)

11.1.1.2 Add an appropriate volume of surrogate compound solution.

11.1.1.2 Add 60 mL of methylene chloride to the sample bottle, seal, and shake 30 s to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 min with periodic venting to release excess pressure. Wait at least 10 min to allow the organic layer to separate from the water phase. If the emulsion interface between layers is more than one-third the volume of the solvent layer, use mechanical techniques (such as stirring, filtration of emulsion through glass wool, or centrifugation) to complete phase separation. Collect the methylene chloride extract in a 250-mL Erlenmeyer flask. Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

11.1.1.3 Assemble a Kurderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask.

11.1.1.4 Pour the combined extract into a solvent-rinsed drying column containing about 10 cm of anhydrous sodium sulfate. Rinse the Erlenmeyer flask with a 20 to 30 mL portion of methylene chloride, and add the rinse to the drying column. Collect the combined extract in the K-D concentrator.

11.1.1.5 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top. Place the K-D apparatus on a hot water bath (60-65°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15-20 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min.

11.1.1.6 Momentarily remove the Snyder column, add 50 mL of hexane and a new boiling chip, and reattach the Snyder column. Increase the temperature of the hot water bath to about 80°C. Concentrate the extract to approximately 10 mL as in Sect. 11.1.1.5, except use hexane to prewet the column. Elapsed time of concentration should be 5-10 min.

11.1.1.7 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of hexane. A 5-mL syringe is recommended for this operation. Stopper the concentrator tube and store refrigerated if further processing will not be performed within a few hours. If the extract will be stored longer than two days, transfer it to a Teflon-sealed screw-cap vial.

11.1.1.8 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11.1.2 Soil/Sediment Samples -- Appropriate extraction procedures to be specified when results of ongoing experiments are obtained.

11.2 Sulfur Removal -- Elemental sulfur can be removed by the procedure described below. (Sulfur is not expected to be a problem in water sample extracts but sulfur removal is recommended for soil/sediment sample extracts.)

11.2.1 Transfer the extract to a 50-mL clear glass bottle or vial with a Teflon-lined screw cap. Rinse the extract container wtih 1.0 mL of hexane, adding the rinse to the 50-mL bottle.

11.2.2 Add 1 mL of Tetrabutylammonium-sulfite reagent and 1 mL 2-propanol, cap the bottle, and shake for at least 1 min. If the sample is colorless or if the initial color is unchanged, and if clear crystals (precipitated sodium sulfite) are observed, sufficient sodium sulfite is present. If the precipitated sodium sulfite disappears, add more crystalline sodium sulfite in approximately 100-mg portions until a solid residue remains after repeated shaking.

11.2.3 Add 5 mL of distilled water and shake for at least 1 min. Allow the sample to stand for 5-10 min and remove the hexane layer (top) for analysis. Dry the extract by passing it through a 10-cm column containing hexane-washed sodium sulfate. Rinse the sodium sulfate with about 30 mL of hexane and add this hexane to the extract. Concentrate the extract to approximately 10 mL with a K-D apparatus. Store in a refrigerator if GC/MS analysis is not to be performed within a few hours.

## 11.3 GC/MS ANALYSIS

11.3.1 Remove the sample extract or blank from storage and allow it to warm to ambient laboratory temperature if necessary. With a stream of dry, filtered nitrogen, reduce the extract/blank volume to the appropriate volume, depending on anticipated analyte concentrations. Add an appropriate volume of the appropriate internal standard stock solution.

11.3.1.1 Internal standard concentration for full-range data acquisition = 7.5 ng/uL of extract.

11.3.1.2 Internal standard concentration for SIM data acquisition = 0.75 ng/uL of extract.

11.3.2 Inject a 1-uL or 2-uL aliquot of the blank/sample extract into the GC operated under conditions used to produce acceptable results during calibration.

11.3.3 Acquire mass spectral data with either full-range data acquisition conditions or SIM conditions, as appropriate. Use the same data acquisition time and MS operating conditions previously used to determine response factors.

11.3.4 Examine data for saturated ions in mass spectra of target compounds, if saturation occurred, dilute and reanalyze the extract after the quantity of the internal standards is adjusted appropriately.

11.3.5 For each internal standard, determine that the area measured in the sample extract has not decreased by >30% from the area measured during the most recent previous analysis of a calibration solution or by >50% from the mean area measured during initial calibration. If either criterion is not met, remedial action must be taken to improve sensitivity, and the sample extract must be reanalyzed.

## 11.4 IDENTIFICATION PROCEDURES

11.4.1 Using the ions shown in Tables 7a-7c for PCBs or Table 9 for pesticides, examine ion current profiles (ICPs) to locate internal standards, surrogate compounds, pesticide analytes, and PCBs for each isomer group. Use the RRT data in Table 9 as guidelines for location of pesticide analytes and the RRT window data in Table 8 as guidelines for location of PCB isomers. (A reverse search software routine can be used to locate compounds of concern.)

### 11.4.2 Full-Range Data

11.4.2.1 Examine each pesticide and PCB candidate spectrum after background correction routines have been applied. Compare the candidate spectrum with the appropriate standard spectrum measured during calibration. Verify the absence of any ions with mass greater than the highest mass possible for the compound of concern. (Ions in PCB $M^+$ ion clusters are shown in Table 12.)

11.4.2.2 Obtain integrated abundance areas for quantitation and confirmation ions.

11.4.3 SIM Data -- Obtain appropriate selected ion current profiles (SICPs) for IS quantitation and confirmation ions, for each ion monitored to detect pesticides and the surrogate compounds (Table 9), and for the quantitation and confirmation ions for each PCB isomer group.

11.4.4 PCB Analytes

11.4.4.1 For all PCB candidates, confirm the presence of an $(M-70)^+$ ion cluster by examining ICPs or spectra for at least one of the most intense ions in the appropriate ion cluster.

11.4.4.2 For $Cl_3$-$Cl_7$ isomer groups, examine ICPs or spectra for intense $(M+70)^+$ ions that would indicate a coeluting PCB containing two additional chlorines. (GC retention time data show that this is not a potential problem for other PCB isomer groups; see Figure 2.) If this interference occurs, a correction can be made. Obtain and record the area for the appropriate ion (Table 12) for the candidate PCB isomer group. Use the information in Table 13 to correct the measured abundance of $M^+$. For example, if a $Cl_7$-PCB and a $Cl_5$-PCB candidate coelute, the $Cl_7$-PCB will contribute to the ion measured for m/z 326 and m/z 324, the quantitation and confirmation ions, respectively, for a $Cl_5$-PCB. Obtain and record the area for m/z 322 (the lowest mass ion in the $(M+-70)^+$ ion cluster of a $Cl_5$-PCB fragment produced by a $Cl_7$-PCB). To determine the m/z 326 and m/z 324 areas produced by the $Cl_5$ PCB, calculate the $Cl_7$-PCB contribution to each and subtract it from the measured area. In this example, 164% of the area measured for m/z 322 should be subtracted from the area measured for m/z 324, and 108% of the m/z 322 area should be subtracted from the area measured for m/z 326 (Table 13).

11.4.4.3 For $Cl_2$-$Cl_8$-PCB candidates, examine ICPs or spectra for intense $(M+35)^+$ ions that would indicate a coeluting PCB containing one additional chlorine. This coelution causes interferences because of the natural abundance of $^{13}C$. (This interference will be small and can be neglected except when measuring the area of a small amount of a PCB coeluting with a large amount of another PCB containing one more chlorine.) To correct for this interference, obtain and record the area for the appropriate ion (Table 14) from the $(M-1)^+$ ion cluster, and subtract 13.5% of the area measured for the $(M-1)^+$ ion from the measured area of the quantitation ion. For example, for $Cl_5$-PCB candidates, obtain and record the area for m/z 325; subtract 13.5% of that area from the measured area of m/z 326.

11.4.5 All Analytes -- Use ICP data to calculate the ratio of the measured peak areas of the quantitation ion and confirmation ion(s), and compare to the acceptable ratio (Table 9 for pesticides and Table 12 for PCBs). If acceptable ratios are not obtained, a coeluting or partially coeluting compound may be interfering. Examination of data from several scans may provide information that will allow application of additional background corrections to improve the ion ratio.

## 11.5. IDENTIFICATION CRITERIA

### 11.5.1 Internal Standards

11.5.1.1 Chrysene-$d_{12}$ — the abundance of m/z 241 relative to m/z 240 must be $\geq 15\%$ and $\leq 25\%$, and these ions must maximize simultaneously. The area measured for m/z 240 must be within 30% of the area measured during the most recent calibration.

11.5.1.2 Phenanthrene-$d_{10}$ — the abundance of m/z 189 relative to m/z 188 must be $\geq 10\%$ and $\leq 22\%$, and these ions must maximize simultaneously. The area measured for m/z 188 must be within 30% of the area measured during the most recent acceptable calibration.

11.5.1.3 Retention time must be within ±10 s of that observed during the most recent acceptable calibration.

### 11.5.2 Full-Range Data for Pesticide Analytes and Surrogate Compounds

11.5.2.1 Retention time of the sample component must be within $\underline{t}$ s of the time observed for that same compound when a calibration solution was analyzed. Calculate the value of $\underline{t}$ with the equation, $t = (RT)^{1/3}$, where RT = observed retention time (in seconds) of the compound during the last previous acceptable calibration.

11.5.2.2 All ions with relative abundance >10% in the mass spectrum must be present in the mass spectrum of the candidate sample component; a molecular ion with relative abundance >2% in the standard spectrum must be present in the candidate spectrum.

11.5.2.3 The ion that was the most abundant (base peak) in the standard spectrum must also be the base peak in the candidate spectrum.

11.5.2.4 For all ions with relative abundance >20% in the standard spectrum, the relative abundance in the candidate spectrum must not vary by more than ±15% in percentage units (i.e., if 50% in standard, must be $\geq 35\%$ and $\leq 65\%$).

11.5.2.5 Ions with relative abundance >10% in the candidate spectrum but not present in the standard spectrum must be considered and accounted for by the analyst. When data processing software is used to obtain candidate spectra, both processed and unprocessed spectra must be evaluated.

### 11.5.3 SIM Data for Pesticide Analytes and Surrogate Compounds

11.5.3.1 Absolute retention time of each surrogate compound and pesticide candidate must be within 10 s of that measured during the last previous acceptable calibration.

11.5.3.2 All ions monitored for each compound (Table 9) must be present and must maximize simultaneously.

11.5.3.3 In a spectrum averaged across a GC peak and with background correction, if necessary, the most abundant ion must correlate with Table 9 data.

11.5.3.4 Observed relative abundances of the monitored ions must meet the following criteria:

Aldrin — m/z 263 = >20% and m/z 265 = >13%
BHC (each isomer) -- m/z 183 = 70-95% of m/z 181
$^{13}C_6$-gamma-BHC — m/z 189 = 75-90% of m/z 187
Chlordane (alpha and gamma) -- m/z 375 = 75-99%
4,4'-DDE — m/z 248 = 45-85%
4,4'-DDD and 4,4'-DDT — m/z 237 = 45-85%
$^{13}C_{12}$-4,4'-DDT — m/z 249 = 45-85%
Dieldrin — m/z 263 = >3% and m/z 108 = >8%
Endosulfan I and II — m/z 339 = >30% and m/z 341 = >20%
Endosulfan sulfate — m/z 274 = 60-95%
Endrin — m/z 263 = ≥50%
Endrin aldehyde -- m/z 345 = ≥10%
Endrin ketone -- m/z 317 = ≥30%
Heptachlor — m/z 272 = >30% and m/z 274 = >20%
Heptachlor epoxide — m/z 353 = >60%
Methoxychlor — m/z 228 = 3-30%
Nonachlor -- m/z 407 = 65-95%

11.5.4 Full-Range and SIM Data for PCBs

11.5.4.1 Absolute retention times of surrogate compounds must be within ±10 s of that measured during the last previous continuing calibration check.

11.5.4.2 Quantitation and confirmation ions for each PCB isomer group must maximize within ±1 scan of each other.

11.5.4.3 The integrated ion current for each quantitation and confirmation ion must be at least three times background noise and must not have saturated the detector.

11.5.4.4 For each PCB isomer group candidate, the ratio of the quantitation ion area to the confirmation ion area must be within limits shown in Table 12; at least one ion in the $(M-70)^+$ ion cluster must be present.

## 12. CALCULATIONS

12.1 From appropriate ICPs of quantitation ions, obtain and record the spectrum number of the chromatographic peak apex and the area of the entire chromatographic peak.

12.2 For PCBs, sum the areas for all isomers identified at each level of chlorination (e.g., sum all quantitation ion areas for $Cl_4$-PCBs).

12.3 Calculate the concentration of each surrogate compound, pesticide candidate, and PCB isomer group using the formula:

$$C_x = (A_x \cdot Q_{is})/(A_{is} \cdot RF \cdot W)$$

where $C_x$ = concentration (micrograms per kilogram or micrograms per liter) of surrogate compound, individual pesticide or a PCB isomer group,

$A_x$ = the area of the quantitation ion for each pesticide analyte/surrogate compound or the sum of quantitation ion areas for all PCB isomers at a particular level of chlorination,

$A_{is}$ = the area of the internal standard quantitation ion, m/z 240 for chrysene-$d_{12}$ or m/z 188 for phenanthrene-$d_{10}$,

$Q_{is}$ = quantity (micrograms) of internal standard added to the extract before GC/MS analysis,

RF = calculated response factor for the surrogate compound, the pesticide standard, or the PCB calibration compound for the isomer group (level of chlorination), and

W = weight (kilograms) of sample extracted. If a liquid sample was extracted, W becomes V, the volume (liters) of water extracted, and concentration units become micrograms per liter.

12.3.1 Use the grand mean RF calculated during Initial Calibration. CAUTION: For PCB analyses with automated data interpretation a linear fit algorithm will produce erroneous concentration data.

12.3.2 For pesticides eluting before heptachlor epoxide, use the RF relative to phenanthrene-$d_{10}$; for heptachlor expoxide and later eluting pesticides, use the RF relative to chrysene-$d_{12}$. For PCBs, use the RF relative to chrysene-$d_{12}$ unless an interference makes the use of the RF relative to phenanthrene-$d_{10}$ necessary.

12.4 Estimation of the Concentration of Technical Chlordane. Technical chlordane is a mixture that contains alpha-chlordane (about 13% by weight), gamma-chlordane (about 18% by weight), heptachlor (about 8%), chlordane (three isomers; about 19%) and a variety of side reaction products (including nonachlor isomers) from chlorination of chlordane. Alpha-chlordane is readily converted to gamma-chlordane, which is persistent in environmental samples. Another persistent component is trans-nonachlor. The presence of gamma-chlordane and trans-nonachlor, with or without alpha-chlordane and heptachlor) indicates that technical chlordane was once present in the sample. Therefore the sum of measured concentrations of alpha-chlordane and gamma-chlordane can be used to estimate the original concentration of technical chlordane.

$$C_{tc} = (C_a + C_g)/0.31$$

where $C_a$ = measured concentration of alpha-chlordane,
$C_g$ = measured concentration of gamma-chlordane, and
$C_{tc}$ = estimated concentration of technical chlordane.

12.5 Report calculated values to two significant figures.

12.6 When samples of known composition or fortified samples are analyzed, calculate the percent method bias using the equation:

$$B = 100\ (C_s - C_t)/\ C_t$$

where $C_s$ = measured concentration (in micrograms per kilogram or micrograms per liter),
$C_t$ = theoretical concentration (i.e., the quantity added to the sample aliquot/weight or volume of sample aliquot).

Note: The bias value retains a positive or negative sign.

## 13. AUTOMATED IDENTIFICATION AND MEASUREMENT

Special software can be used for automated identification and measurement of PCBs (8) and pesticides. Unprocessed GC/MS data are handled without human interaction with the software operating on the dedicated computer. A concentration for each pesticide and each PCB isomer group is calculated automatically. Contact EMSL-Cincinnati for further information.

## 14. METHOD PERFORMANCE

To obtain single laboratory accuracy and precision data for method analytes, replicate 1-L aliquots of reagent water and river water fortified with known amounts of analytes were extracted and analyzed. Automated procedures were used to identify and measure method analytes in 2-uL aliquots of 1-mL extracts. Because a sufficient quantity of individual PCB congeners was not available, Aroclor mixtures were used to fortify water samples. This is not desirable, because individual PCBs in Aroclors vary in concentration. As Aroclor concentrations decrease in a sample extract, an increasing number of components will fall below the detection limit and will not be identified and measured. In addition, insufficient data are available about Aroclor composition to assess accuracy of isomer group measurements or to assess MDLs for PCBs when Aroclors are used to fortify samples.

14.1 Medium Level Reagent Water Extracts -- Five aliquots of reagent water fortified with each individual pesticide at a concentration of 10 ug/L and Aroclors 1221, 1242, 1254, and 1268 at concentrations of 5 ug/L, 50 ug/L, 50 ug/L and 25 ug/L, respectively, were extracted and analyzed. Method bias for individual pesticides ranged from -10% to +18% with a mean method bias of +2% for all 21 pesticides (Table 15). For individual pesticides, RSDs of measured concentration ranged from 0.61% for endrin ketone to 9.8% for endrin aldehyde. No true values are known for concentrations of PCB isomer groups in Aroclors, but the mean measured total PCB concentration was 110 ug/L (RSD 2.9%), which indicated a method bias of -15%. For individual isomer groups, RSDs of mean measured concentrations ranged from 3.9% to 16%.

14.2 Low Level Reagent Water Extract -- Reagent water was fortified with each pesticide at a concentration of 3 ug/L and a total PCB concentration of 27 ug/L (Aroclors 1221, 1 ug/L; 1242, 10 ug/L; 1254, 10 ug/L; and 1268, 6 ug/L). When seven replicate extracts were analyzed, method bias for individual pesticides ranged from -17% to +20% with a mean method bias of -2% (Table 15). An MDL was calculated for each pesticide using the equation relating the standard deviation of the seven replicate measurement and Student's t value for a one-tailed test at the 99% confidence level with n-1 degrees of freedom (1). With this calculation, MDL is defined as the minimum concentration that can be measured and reported with 99% confidence that the value is above zero. The excellent precision achieved with these measurements resulted in unrealistically low MDLs ranging from 0.2 to 0.8 ug/L for pesticide analytes (Table 15). A PCB MDL is an individual congener characteristic and cannot be determined with samples fortified with Aroclor mixtures. Estimates of MDLs for individual components of PCB isomer groups were obtained by proportioning the total quantity measured for each isomer group among individual measured isomers. The estimated MDL values for individual PCBs also were unrealistically low (0.01-0.1 ug/L) because of the excellent precision of measurements. A more realistic statement of detection limits for pesticides and PCBs can be found in Sect. 1.2.

14.3 River Water Extracts -- Five aliquots of river water fortified with each pesticide at a concentration of 5 ug/L and total PCB concentration of 70 ug/L (Aroclors 1221, 2 ug/L; 1242, 30 ug/L; 1254, 30 ug/L; and 1268, 8 ug/L) were extracted and analyzed. Method bias for individual pesticides ranged from -30% to +8% with a mean of -8% (Table 15). The excellent precision of measured pesticide PCB isomer group concentrations was indicated by RSDs ranging from 1.6% to 7.5%. The mean measured total PCB concentration of 51 ug/L (RSD 2.5%) indicated a method bias of -27%.

## 15. REFERENCES

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Table 1. Recommended GC Operating Conditions

| | |
|---|---|
| Column Type: | SE-54 or DB-5 |
| Film Thickness: | 0.25 um |
| Column Dimensions: | 30 m X 0.32 mm |
| Helium Linear Velocity: | 28-29 cm/sec at 250°C |
| Temperature Program for Splitless Injection: | |
| o Full-range data acquisition for PCBs and pesticides (Analysis time = approx. 50 min) | Inject at 80°C and hold 1 min; increase at 30°/min to 160°C and hold 1 min; increase at 3°/min to 310°C.<br>or<br>Inject at 80°C and hold 1 min; heat rapidly to 160°C and hold 1 min; increase at 3°/min to 310°C. |
| o SIM data acquisition for PCBs (Analysis time = approx. 25 min) | Inject at 45°C and hold 1 min; increase at 20°/min to 150°C and hold 1 min; increase at 10°/min to 310°C. |
| o SIM data acquisition for pesticides (Analysis time = approx. 30 min) | Inject at 80°C and hold 1 min; increase at 30°/min to 160°C and hold 1 min; increase at 3°/min to 250°C; hold past elution time of methoxychlor. |

Table 2. PCB Congeners Used as Calibration Standards

| PCB Isomer Group | Congener Number[a] | Chlorine Substitution |
|---|---|---|
| Concentration Calibration Standard | | |
| Monochlorobiphenyl | 1 | 2 |
| Dichlorobiphenyl | 5 | 2,3 |
| Trichlorobiphenyl | 29 | 2,4,5 |
| Tetrachlorobiphenyl | 50 | 2,2',4,6 |
| Pentachlorobiphenyl | 87 | 2,2',3,4,5' |
| Hexachlorobiphenyl | 154 | 2,2',4,4',5,6' |
| Heptachlorobiphenyl | 188 | 2,2',3,4',5,6,6' |
| Octachlorobiphenyl | 200 | 2,2',3,3',4,5',6,6' |
| Nonachlorobiphenyl[b] | - | —— |
| Decachlorobiphenyl | 209 | 2,2',3,3',4,4',5,5',6,6' |
| Retention Time Calibration Standards | | |
| Tetrachlorobiphenyl | 77 | 3,3',4,4' |
| Pentachlorobiphenyl | 104 | 2,2',4,6,6' |
| Nonachlorobiphenyl | 208 | 2,2',3,3',4,5,5',6,7' |

[a] Numbered according to the system of Ballschmiter and Zell (2).

[b] Decachlorobiphenyl is used as the calibration congener for both nona- and decachlorobiphenyl isomer groups.

Table 3. Scheme for Preparation of PCB Primary Dilution Standard

| PCB Cong. | Isomer Group | Stock Sol. Conc. mg/mL | Proportion for Primary Dil. Sol. | Primary Dil. Std. Conc. ng/uL |
|---|---|---|---|---|
| #1 | $Cl_1$ | 1.0 | 1 part | 50 |
| #5 | $Cl_2$ | 1.0 | 1 part | 50 |
| #29 | $Cl_3$ | 1.0 | 1 part | 50 |
| #50 | $Cl_4$ | 1.0 | 2 parts | 100 |
| #87 | $Cl_5$ | 1.0 | 2 parts | 100 |
| #154 | $Cl_6$ | 1.0 | 2 parts | 100 |
| #188 | $Cl_7$ | 1.0 | 3 parts | 150 |
| #200 | $Cl_8$ | 1.0 | 3 parts | 150 |
| #209 | $Cl_{10}$ | 1.0 | 5 parts | 250 |
|  |  | Total | 20 parts |  |

**Table 4. Composition and Approximate Concentrations of Calibration Solutions for Full-Range Data Acquisition**

| Analyte/Int. Std./ Surrogate Compound | Concentration (ng/uL) | | | | |
|---|---|---|---|---|---|
| | CAL 1 | CAL 2 | CAL 3 | CAL 4 | CAL 5 |
| **PCB Cal. Congeners** | | | | | |
| $Cl_1$ (#1) | 0.5 | 2.5 | 5 | 10 | 25 |
| $Cl_2$ (#5) | 0.5 | 2.5 | 5 | 10 | 25 |
| $Cl_3$ (#29) | 0.5 | 2.5 | 5 | 10 | 25 |
| $Cl_4$ (#50) | 1 | 5 | 10 | 20 | 50 |
| $Cl_5$ (#87) | 1 | 5 | 10 | 20 | 50 |
| $Cl_6$ (#154) | 1 | 5 | 10 | 20 | 50 |
| $Cl_7$ (#188) | 1.5 | 7.5 | 15 | 30 | 75 |
| $Cl_8$ (#200) | 1.5 | 7.5 | 15 | 30 | 75 |
| $Cl_{10}$ (#209) | 2.5 | 12.5 | 25 | 50 | 125 |
| **Pesticides** | | | | | |
| Aldrin | 1 | 5 | 10 | 20 | 50 |
| BHC, each isomer | 1 | 5 | 10 | 20 | 50 |
| Chlordane, each isomer | 1 | 5 | 10 | 20 | 50 |
| 4,4'-DDD | 1 | 5 | 10 | 20 | 50 |
| 4,4'-DDE | 1 | 5 | 10 | 20 | 50 |
| 4,4'-DDT | 1 | 5 | 10 | 20 | 50 |
| Dieldrin | 1 | 5 | 10 | 20 | 50 |
| Endosulfan I | 2 | 10 | 20 | 40 | 100 |
| Endosulfan II | 2 | 10 | 20 | 40 | 100 |
| Endosulfan sulfate | 2 | 10 | 20 | 40 | 100 |
| Endrin | 1 | 5 | 10 | 20 | 50 |
| Endrin aldehyde | 1 | 5 | — | 20 | 50 |
| Endrin ketone | 1 | 5 | 10 | 20 | 50 |
| Heptachlor | 1 | 5 | 10 | 20 | 50 |
| Heptachlor epoxide | 1 | 5 | 10 | 20 | 50 |
| Methoxychlor | 1 | 5 | 10 | 20 | 50 |
| Nonachlor, each isomer | 1 | 5 | 10 | 20 | 50 |
| **Internal Standards** | | | | | |
| Chrysene-$d_{12}$ | 7.5 | 7.5 | 7.5 | 7.5 | 7.5 |
| Phenanthrene-$d_{10}$ | 7.5 | 7.5 | 7.5 | 7.5 | 7.5 |
| **Surrogate Compounds** | | | | | |
| $^{13}C_6$-gamma BHC | 1 | 5 | 10 | 20 | 50 |
| $^{13}C_{12}$-4,4'-DDT | 1 | 5 | 10 | 20 | 50 |

### Table 5a. Composition and Approximate Concentrations of Calibration Solutions for SIM Data Acquisition for PCB Determinations

| Compound | Concentration (ng/uL) | | | | |
|---|---|---|---|---|---|
| | CAL 1 | CAL 2 | CAL 3 | CAL 4 | CAL 5 |
| Cal. Congeners | | | | | |
| $Cl_1$ (#1) | 0.1 | 0.5 | 1 | 2 | 5 |
| $Cl_2$ (#5) | 0.1 | 0.5 | 1 | 2 | 5 |
| $Cl_3$ (#29) | 0.1 | 0.5 | 1 | 2 | 5 |
| $Cl_4$ (#50) | 0.2 | 1.0 | 2 | 4 | 10 |
| $Cl_5$ (#87) | 0.2 | 1 | 2 | 4 | 10 |
| $Cl_6$ (#154) | 0.2 | 1 | 2 | 4 | 10 |
| $Cl_7$ (#188) | 0.3 | 1.5 | 3 | 6 | 15 |
| $Cl_8$ (#200) | 0.3 | 1.5 | 3 | 6 | 15 |
| $Cl_{10}$ (#209) | 0.5 | 2.5 | 5 | 10 | 25 |
| RT Congeners | | | | | |
| $Cl_4$ (#77) | 0.2 | 1 | 2 | 4 | 10 |
| $Cl_5$ (#104) | 0.2 | 1 | 2 | 4 | 10 |
| $Cl_9$ (#208) | 0.4 | 2 | 4 | 8 | 20 |
| Internal Standards | | | | | |
| Chrysene-$d_{12}$ | 0.75 | 0.75 | 0.75 | 0.75 | 0.75 |
| Phenanthrene-$d_{10}$ | 0.75 | 0.75 | 0.75 | 0.75 | 0.75 |
| Surrogate Compounds | | | | | |
| $^{13}C_6$-gamma-BHC | 0.2 | 1 | 2 | 4 | 10 |
| $^{13}C_{12}$-4,4'-DDT | 0.2 | 1 | 2 | 4 | 10 |

Table 5b. Composition and Approximate Concentrations of Calibration Solutions for SIM Data Acquisition for Pesticide Determinations

| Analyte/Internal Std/ Surrogate Compound | Concentration (ng/uL) | | | | |
|---|---|---|---|---|---|
| | CAL 1 | CAL 2 | CAL 3 | CAL 4 | CAL 5 |
| Pesticide Analytes | | | | | |
| Aldrin | 0.2 | 1 | 2 | 5 | 10 |
| BHC, each isomer | 0.2 | 1 | 2 | 5 | 10 |
| Chlordane, each isomer | 0.2 | 1 | 2 | 5 | 10 |
| 4,4'-DDD | 0.2 | 1 | 2 | 5 | 10 |
| 4,4'-DDE | 0.2 | 1 | 2 | 5 | 10 |
| 4,4'-DDT | 0.2 | 1 | 2 | 5 | 10 |
| Dieldrin | 0.2 | 1 | 2 | 5 | 10 |
| Endosulfan I | 0.4 | 2 | 4 | 10 | 20 |
| Endosulfan II | 0.4 | 2 | 4 | 10 | 20 |
| Endosulfan sulfate | 0.2 | 1 | 2 | 5 | 10 |
| Endrin | 0.2 | 1 | 2 | 5 | 10 |
| Endrin aldehyde | 0.2 | 1 | - | 5 | 10 |
| Endrin ketone | 0.2 | 1 | 2 | 5 | 10 |
| Heptachlor | 0.2 | 1 | 2 | 5 | 10 |
| Heptachlor epoxide | 0.2 | 1 | 2 | 5 | 10 |
| Methoxychlor | 0.2 | 1 | 2 | 5 | 10 |
| Nonachlor, each isomer | 0.2 | 1 | 2 | 5 | 10 |
| Internal Standards | | | | | |
| Chrysene-$d_{12}$ | 0.75 | 0.75 | 0.75 | 0.75 | 0.75 |
| Phenanthrene-$d_{10}$ | 0.75 | 0.75 | 0.75 | 0.75 | 0.75 |
| Surrogate Compounds | | | | | |
| $^{13}C_6$-gamma-BHC | 0.2 | 1 | 2 | 5 | 10 |
| $^{13}C_{12}$-4,4'-DDT | 0.2 | 1 | 2 | 5 | 10 |

Table 6. Criteria for DFTPP Spectrum

| m/z | Relative Abundance |
|---|---|
| 127 | 40-60% |
| 197 | <1% |
| 198 | 100% (Base Peak) |
| 199 | 5-9% |
| 275 | 10-30% |
| 365 | >1% |
| 441 | Present and <m/z 443 |
| 442 | >40% |
| 443 | 17-23% of m/z 442 |

Table 7a. Ions for Selected Ion Monitoring to Determine PCBs by Acquiring Data for Four Sets of $\leq 35$ Ions Each

| PCB Isomer Group/ Int.Std./Surr.Cmpd. | Nominal Mol. Wt. | Mass or Range to be Monitored | No. of Ions | Ion Sets |  |  |  |
|---|---|---|---|---|---|---|---|
|  |  |  |  | #1 | #2 | #3 | #4 |
| Monochlorobiphenyls | 188 | 152; 186–190 | 6 | 6 |  |  |  |
| Dichlorobiphenyls | 222 | 220–224 | 5 | 5 |  |  |  |
| Trichlorobiphenyls | 256 | 254–260 | 7 | 7 | 7 | 1[a] |  |
| Tetrachlorobiphenyls | 290 | 288–294 | 7 | 7 | 7 | 1[b] |  |
| Pentachlorobiphenyls | 324 | 322–328 | 7 |  | 7 | 7 |  |
| Hexachlorobiphenyls | 358 | 356–362 | 7 |  | 6[c] | 7 | 7 |
| Heptachlorobiphenyls | 392 | 390–396 | 7 |  |  | 6[d] | 7 |
| Octachlorobiphenyls | 426 | 424–430 | 7 |  |  |  | 7 |
| Nonachlorobiphenyls | 460 | 460–466 | 7 |  |  |  | 7 |
| Decachlorobiphenyl | 494 | 496–500 | 5 |  |  |  | 5 |
| Chrysene-$d_{12}$ | 240 | 240–241 | 2 |  |  |  | 2 |
| Phenanthrene-$d_{10}$ | 188 | 188–189 | 2 | 2[e] |  |  |  |
| $^{13}C_6$-gamma-BHC | 294 | 187, 189 | 2 | 2[f] |  |  |  |
| $^{13}C_{12}$-4,4'-DDT | 364 | 247; 249 | 2 |  |  | 2 |  |
|  |  |  | Total # ions | 25 | 27 | 24 | 35 |

[a] Monitor m/z 254 to confirm presence of $(M-70)^+$ for $Cl_5$-PCBs.

[b] Monitor m/z 288 to confirm presence of $(M-70)^+$ for $Cl_6$-PCBs.

[c] Begin range at m/z 357 in Ion Set #2.

[d] Begin range at m/z 391 in Ion Set #3.

[e] M/z 188 and 189 included among ions used to detect and measure monochlorobiphenyls.

[f] M/z 187 and 189 included among ions used to detect and measure monochlorobiphenyls.

Table 7b. Ions for Selected Ion Monitoring to Determine PCBs by Acquiring Data for Five Sets of ≤20 Ions Each

| Ion Set | Isomer Group/ IS/Surrogate | Quant. Ion | Confirm. Ions | M-70 Ions | M+70 Ions | M+35 Ions | Ion Measured[a] for Correction | |
|---|---|---|---|---|---|---|---|---|
| 1 | $Cl_1$ | 188 | 190 | 152,153[b] | 256,258 | 222,224 | - | - |
| | $Cl_2$ | 222 | 224 | 152,153,186,188[c] | 290,292,294 | 256,258 | - | 221 |
| | $Cl_3$ | 256 | 258 | 186,188 | - | 290,292,294 | - | 255 |
| | $Cl_4$ | 292 | 290,294 | 220,222 | - | - | - | - |
| | $^{13}C_6$-gamma-BHC | 187 | 189 | - | - | - | - | - |
| | Phenanthrene-$d_{10}$ | 188 | 189 | - | - | - | - | - |
| 2 | $Cl_3$ | 256 | 258 | 186,188 | 324,326,328 | 290,292,294 | 254 | 255 |
| | $Cl_4$ | 292 | 290,294 | 220,222 | 360,362 | 324,326,328 | 288 | 289 |
| | $Cl_5$ | 326 | 324,328 | 254,256,258 | - | 360,362 | - | 323 |
| | $Cl_6$ | 360 | 358,362 | 288,290,292 | - | - | - | - |
| 3 | $Cl_5$ | 326 | 324,328 | 254,256 | 392,394,396,398 | 360,362 | 322 | 323 |
| | $Cl_6$ | 360 | 358,362 | 288,290 | - | 392,394,396,398 | - | 357 |
| | $Cl_7$ | 394 | 392,396 | 322,324,326 | - | - | - | - |
| | $^{13}C_{12}$-4,4'-DDT | 247 | 249 | - | - | - | - | - |
| 4 | $Cl_6$ | 360 | 358,362 | 288,290 | 426,428,430,432 | 392,394,396 | 356 | 357 |
| | $Cl_7$ | 394 | 392,396,398 | 322,324 | - | 428,430,432 | - | 391 |
| | $Cl_8$ | 430 | 428,432 | 356,358,360 | - | - | - | - |
| | Chrysene-$d_{12}$ | 240 | 241 | - | - | - | - | - |
| 5 | $Cl_8$ | 430 | 426,428,432 | 356,358,360 | 494,496,498,500 | 462,464,466 | - | 425 |
| | $Cl_9$ | 464 | 460,462,466 | 390,392,394 | - | 496,498,500 | - | - |
| | $Cl_{10}$ | 498 | 494,496,500 | 424,426,428,430 | - | - | - | - |

[a] See Tables 12-13.
[b] $Cl_1$-PCBs lose HCl.
[c] Some $Cl_2$-PCBs lose $Cl_2$ and some lose HCl.

Table 7c. Ions for Selected Ion Monitoring to Determine PCBs by Acquiring Data for Five Ion Sets of $\leq$20 Ions

| Ion Set No. 1[a] | Ion Set No. 2[b] | Ion Set No. 3[c] | Ion Set No. 4[d] | Ion Set No. 5[e] |
|---|---|---|---|---|
| 152 | 186 | 247 | 240 | 356 |
| 153 | 188 | 249 | 241 | 358 |
| 186 | 220 | 254 | 288 | 360 |
| 187 | 222 | 256 | 290 | 390 |
| 188 | 254 | 288 | 322 | 392 |
| 189 | 255 | 290 | 324 | 394 |
| 190 | 256 | 322 | 326 | 424 |
| 220 | 258 | 323 | 356 | 425 |
| 221 | 288 | 324 | 357 | 426 |
| 222 | 289 | 326 | 358 | 428 |
| 224 | 290 | 328 | 360 | 430 |
| 255 | 292 | 357 | 362 | 432 |
| 256 | 294 | 358 | 391 | 462 |
| 258 | 323 | 360 | 392 | 464 |
| 290 | 324 | 362 | 394 | 466 |
| 292 | 326 | 392 | 396 | 496 |
| 294 | 328 | 394 | 398 | 498 |
|  | 358 | 396 | 428 | 499 |
|  | 360 | 398 | 430 | 500 |
|  | 362 |  | 432 | 502 |
| 17 ions | 20 ions | 19 ions | 20 ions | 20 ions |

[a] Ions to identify and measure $Cl_1$-$Cl_4$-PCBs, phenanthrene-$d_{10}$, and $^{13}C_6$-gamma-BHC.

[b] Ions to identify and measure $Cl_3$-$Cl_6$-PCBs.

[c] Ions to identify and measure $Cl_5$-$Cl_7$-PCBs and $^{13}C_{12}$-4,4'-DDT.

[d] Ions to identify and measure $Cl_6$-$Cl_8$-PCBs and chrysene-$d_{12}$.

[e] Ions to identify and measure $Cl_8$-$Cl_{10}$-PCBs.

Table 8. Retention Time Data for PCB Isomer Groups and Calibration Congeners

| Isomer Group | Approximate RRT Range[a] | Cal. Cong. Number | Cal. Cong. RRT[a] |
|---|---|---|---|
| Monochlorobiphenyls | 0.30-0.35 | 1 | 0.30 |
| Dichlorobiphenyls | 0.38-0.50 | 5 | 0.43 |
| Trichlorobiphenyls | 0.46-0.64 | 29 | 0.54 |
| Tetrachlorobiphenyls | 0.55-0.82 | 50 | 0.56 |
| Pentachlorobiphenyls | 0.64-0.92 | 87 | 0.80 |
| Hexachlorobiphenyls | 0.75-1.1 | 154 | 0.82 |
| Heptachlorobiphenyls | 0.88-1.2 | 188 | 0.88 |
| Octachlorobiphenyls | 0.99-1.21 | 200 | 1.03 |
| Nonachlorobiphenyls | 1.16-1.28 | - | - |
| Decachlorobiphenyl | 1.3 | 209 | 1.3 |

[a] Retention time relative to chrysene-$d_{12}$ with a 30 m X 0.31 mm ID SE-54 fused silica capillary column and the following GC conditions: splitless injection at 80°C; hold for 1 min; heat rapidly to 160°C and hold 1 min; increase at 3°C/min to 310°C.

Table 9. Ions for Selected Ion Monitoring Data Acquisition for Pesticide Analytes, Internal Standards and Surrogate Compounds (Ordered by Retention Time)

| Ion Set | Analyte/Internal Std/ Surrogate Compound (MW) | Approx. RRT | Quant. Ion | Ions (Approximate Relative Abundance) |
|---|---|---|---|---|
| 1 | Alpha-BHC (288) | 0.43 | 219 | 181 (100), 183 (90), 219 (70) |
| | Beta-BHC (288) | 0.47 | 219 | 181 (100), 183 (90), 219 (70) |
| | Gamma-BHC (288) | 0.48 | 219 | 181 (100), 183 (90), 219 (75) |
| | $^{13}C_6$-gamma-BHC (294) | 0.48 | 225 | 187 (100), 189 (90) 225 (80), 227 (40) |
| | Phenanthrene-$d_{10}$ (188) | 0.49 | 188 | 188 (100), 189 (15) |
| | Delta-BHC (288) | 0.51 | 219 | 181 (100), 183 (90), 219 (70) |
| | Heptachlor (370) | 0.58 | 272 | 100 (100), 272 (60), 274 (40) |
| | Aldrin (362) | 0.64 | 263 | 66 (100), 263 (40), 265 (25) |
| 2 | Heptachlor epoxide (386) | 0.70 | 353 | 81 (100), 353 (80), 355 (65) |
| | Gamma-chlordane (406) | 0.74 | 373 | 373 (100), 375 (95) |
| | Endosulfan I (404) | 0.76 | 195 | 195 (100), 339 (50), 341 (35) |
| | Alpha-chlordane (406) | 0.76 | 373 | 373 (100), 375 (95) |
| | Trans-nonachlor (440) | 0.77 | 409 | 409 (100), 407 (85) |
| | Dieldrin (378) | 0.80 | 79 | 79 (100), 263 (10), 108 (15) |
| | 4,4'-DDE (316) | 0.81 | 246 | 246 (100), 248 (65) |
| | Endrin (378) | 0.83 | 81 | 81 (100), 263 (75) |
| | Endosulfan II (404) | 0.85 | 195 | 195 (100), 339 (50), 341 (35) |
| 3 | 4,4'-DDD (318) | 0.87 | 235 | 235 (100), 237 (65), 165 (65) |
| | Endrin aldehyde (378) | 0.88 | 67 | 67 (100), 345 (30) |
| | Endosulfan sulfate (420) | 0.92 | 272 | 272 (100), 274 (80), 387 (50) |
| | 4,4'-DDT (352) | 0.93 | 235 | 235 (100), 237 (65), 165 (65) |
| | $^{13}C_{12}$-4,4'-DDT (364) | 0.93 | 247 | 247 (100), 249 (65) |
| | Endrin ketone (378) | 0.99 | 67 | 67 (100), 317 (50) |
| | Chrysene-$d_{12}$ (240) | 1.00 | 240 | 240 (100), 241 (20) |
| | Methoxychlor (344) | 1.03 | 227 | 227 (100), 228 (15) |

Table 10. Ion Sets for Selected Ion Monitoring of Pesticide Analytes, Internal Standards and Surrogate Compounds (Ordered by Retention Time)

| Ion Set No. 1 | Monitored Compounds | Ion Set No. 2 | Monitored Compounds | Ion Set No. 3 | Monitored Compounds |
|---|---|---|---|---|---|
| 66 | Alpha-BHC | 79 | Heptachlor epoxide | 67 | 4,4'-DDD |
| 100 | Beta-BHC | 81 |  | 165 | Endrin aldehyde |
| 181 | Delta-BHC | 108 | Alpha-chlordane | 227 | Endosulfan sulfate |
| 183 | Gamma-BHC | 195 | Gamma-chlordane | 228 | 4,4'-DDT |
| 187 | $^{13}C_6$-gamma-BHC | 246 | Endosulfan I | 235 | $^{13}C_{12}$-4,4'-DDT |
| 188 | Phenanthrene-$d_{10}$ | 248 | Trans-nonachlor | 237 | Endrin ketone |
| 189 | Heptachlor | 263 | Dieldrin | 240 | Chrysene-$d_{12}$ |
| 219 | Aldrin | 339 | 4,4'-DDE | 241 | Methoxychlor |
| 225 |  | 341 | Endrin | 247 |  |
| 227 |  | 353 | Endosulfan II | 249 |  |
| 263 |  | 355 |  | 272 |  |
| 265 |  | 373 |  | 274 |  |
| 272 |  | 375 |  | 317 |  |
| 274 |  | 407 |  | 345 |  |
|  |  | 409 |  | 387 |  |
| 14 ions, 8 compounds |  | 15 ions, 9 compounds |  | 15 ions | 8 compounds |

Table 11. Known Relative Abundances of Ions in PCB Molecular Ion Clusters[a]

| m/z | Relative Intensity |
|---|---|
| **Monochlorobiphenyls** | |
| 188 | 100 |
| 189 | 13.5 |
| 190 | 33.4 |
| 192 | 4.41 |
| **Dichlorobiphenyls** | |
| 222 | 100 |
| 223 | 13.5 |
| 224 | 66.0 |
| 225 | 8.82 |
| 226 | 11.2 |
| 227 | 1.44 |
| **Trichlorobiphenyls** | |
| 256 | 100 |
| 257 | 13.5 |
| 258 | 98.6 |
| 259 | 13.2 |
| 260 | 32.7 |
| 261 | 4.31 |
| 262 | 3.73 |
| 263 | 0.47 |
| **Tetrachlorobiphenyls** | |
| 290 | 76.2 |
| 291 | 10.3 |
| 292 | 100 |
| 293 | 13.4 |
| 294 | 49.4 |
| 295 | 6.57 |
| 296 | 11.0 |
| 297 | 1.43 |
| 298 | 0.95 |
| **Pentachlorobiphenyls** | |
| 324 | 61.0 |
| 325 | 8.26 |
| 326 | 100 |
| 327 | 13.5 |
| 328 | 65.7 |
| 329 | 8.78 |
| 330 | 21.7 |
| 331 | 2.86 |
| 332 | 3.62 |
| 333 | 0.47 |
| 334 | 0.25 |
| **Hexachlorobiphenyls** | |
| 358 | 50.9 |
| 359 | 6.89 |
| 360 | 100 |
| 361 | 13.5 |
| 362 | 82.0 |
| 363 | 11.0 |
| 364 | 36.0 |
| 365 | 4.77 |
| 366 | 8.92 |
| 367 | 1.17 |
| 368 | 1.20 |
| 369 | 0.15 |
| **Heptachlorobiphenyls** | |
| 392 | 43.7 |
| 393 | 5.91 |
| 394 | 100 |
| 395 | 13.5 |
| 396 | 98.3 |
| 397 | 13.2 |
| 398 | 53.8 |
| 399 | 7.16 |
| 400 | 17.7 |
| 401 | 2.34 |
| 402 | 3.52 |
| 403 | 0.46 |
| 404 | 0.40 |
| **Octachlorobiphenyls** | |
| 426 | 33.4 |
| 427 | 4.51 |
| 428 | 87.3 |
| 429 | 11.8 |
| 430 | 100 |
| 431 | 13.4 |
| 432 | 65.6 |
| 433 | 8.76 |
| 434 | 26.9 |
| 435 | 3.57 |
| 436 | 7.10 |
| 437 | 0.93 |
| 438 | 1.18 |
| 439 | 0.15 |
| 440 | 0.11 |
| **Nonachlorobiphenyls** | |
| 460 | 26.0 |
| 461 | 3.51 |
| 462 | 76.4 |
| 463 | 10.3 |
| 464 | 100 |
| 465 | 13.4 |
| 466 | 76.4 |
| 467 | 10.2 |
| 468 | 37.6 |
| 469 | 5.00 |
| 470 | 12.4 |
| 471 | 1.63 |
| 472 | 2.72 |
| 473 | 0.35 |
| 474 | 0.39 |
| **Decachlorobiphenyl** | |
| 494 | 20.8 |
| 495 | 2.81 |
| 496 | 68.0 |
| 497 | 9.17 |
| 498 | 100 |
| 499 | 13.4 |
| 500 | 87.3 |
| 501 | 11.7 |
| 502 | 50.0 |
| 503 | 6.67 |
| 504 | 19.7 |
| 505 | 2.61 |
| 506 | 5.40 |
| 507 | 0.71 |
| 508 | 1.02 |
| 509 | 0.13 |

[a] Source: Rote and Morris (9)

Table 12. Quantitation, Confirmation, and Interference Check Ions for PCBs, Internal Standards, and Surrogate Compounds

| Analyte/ Internal Std. | Nom. MW | Quant. Ion | Confirm. Ion | Expected Ratio[a] | Accept. Ratio[a] | M-70 Confirm. Ion | Interference Check Ions | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | M+70 | M+35 |
| PCB Isomer Group | | | | | | | | |
| $Cl_1$ | 188 | 188 | 190 | 3.0 | 2.5-3.5 | 152[b] | 256 | 222 |
| $Cl_2$ | 222 | 222 | 224 | 1.5 | 1.3-1.7 | 152 | 292 | 256 |
| $Cl_3$ | 256 | 256 | 258 | 1.0 | 0.8-1.2 | 186 | 326 | 290 |
| $Cl_4$ | 290 | 292 | 290 | 1.3 | 1.1-1.5 | 220 | 360 | 326 |
| $Cl_5$ | 324 | 326 | 324 | 1.6 | 1.4-1.8 | 254 | 394 | 360 |
| $Cl_6$ | 358 | 360 | 362 | 1.2 | 1.0-1.4 | 288 | 430 | 394 |
| $Cl_7$ | 392 | 394 | 396 | 1.0 | 0.8-1.2 | 322 | 464 | 430 |
| $Cl_8$ | 426 | 430 | 428 | 1.1 | 0.9-1.3 | 356 | 498 | 464 |
| $Cl_9$ | 460 | 464 | 466 | 1.3 | 1.1-1.5 | 390 | - | 498 |
| $Cl_{10}$ | 494 | 498 | 500 | 1.1 | 0.9-1.3 | 424 | - | - |
| Internal standards | | | | | | | | |
| Chrysene-$d_{12}$ | 240 | 240 | 241 | 5.1 | 4.3-5.9 | - | - | - |
| Phenanthrene-$d_{10}$ | 188 | 188 | 189 | 6.6 | 6.0-7.2 | - | - | - |
| Surrogate compounds | | | | | | | | |
| $^{13}C_6$-gamma-BHC | 294 | 187 | 189 | 1.0 | 0.8-1.2 | - | - | - |
| $^{13}C_{12}$-4,4'-DDT | 364 | 247 | 249 | 1.5 | 1.3-1.7 | - | - | - |

[a] Ratio of quantitation ion to confirmation ion

[b] Monodichlorobiphenyls lose HCl to produce an ion at m/z 152.

Table 13. Correction for Interference of PCB Containing Two Additional Chlorines

| Candidate Isomer Group | Quant. Ion | Confirm. Ion | Ion Measured to Determine Interference | % of Meas. Ion Area to be Subtracted from Quant Ion Area | % of Meas. Ion Area to be Subtracted from Confirm. Ion Area |
|---|---|---|---|---|---|
| Trichlorobiphenyls | 256 | 258 | 254 | 99% | 33% |
| Tetrachlorobiphenyls | 292 | 290 | 288 | 65% | 131% |
| Pentachlorobiphenyls | 326 | 324 | 322 | 108% | 164% |
| Hexachlorobiphenyls | 360 | 362 | 356 | 161% | 71% |
| Heptachlorobiphenyls | 394 | 396 | 390 | 225% | 123% |

Table 14. Correction for Interference of PCB Containing One Additional Chlorine

| Candidate Isomer Group | Quant. Ion | Ion Measured to Determine Interference | % of Meas. Ion Area to be Subtracted from Quant. Ion Area |
|---|---|---|---|
| Dichlorobiphenyls | 222 | 221 | 13.5% |
| Trichlorobiphenyls | 256 | 255 | 13.5% |
| Tetrachlorobiphenyls | 292 | 289 | 17.4% |
| Pentachlorobiphenyls | 326 | 323 | 22.0% |
| Hexachlorobiphenyls | 360 | 357 | 26.5% |
| Heptachlorobiphenyls | 394 | 391 | 30.9% |
| Octachlorobiphenyls | 430 | 425 | 40.0% |

Table 15. Accuracy and Precision of Automated Measurements of PCBs and Pesticides in Fortified Water Extracts

| Analyte (Meas. Ion) | Medium Level Reagent Water[a] | | | Low Level Reagent Water[b] | | | | Ohio River Water[a] | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | True Conc. ug/L | Mean Meas. Conc., ug/L (RSD, %) | Bias % | True Conc. ug/L | Mean Meas. Conc., ug/L (RSD, %) | Bias % | MDL ug/L | True Conc. ug/L | Mean Meas. Conc., ug/L (RSD, %) | Bias % |
| Aldrin (263) | 10 | 9.6 (3.6) | -4 | 3 | 2.5 (7.2) | -17 | 0.6 | 5 | 4.7 (3.0) | -6 |
| BHC, alpha (219) | 10 | 9.8 (4.3) | -2 | 3 | 2.8 (5.0) | -7 | 0.4 | 5 | 4.7 (1.6) | -6 |
| BHC, beta (219) | 10 | 10.5 (3.6) | +5 | 3 | 3.0 (2.5) | 0 | 0.2 | 5 | 5.1 (2.5) | +2 |
| BHC, gamma (219) | 10 | 10.2 (4.7) | +2 | 3 | 2.9 (5.3) | -3 | 0.5 | 5 | 4.8 (3.8) | -4 |
| BHC, delta (219) | 10 | 9.9 (4.2) | -1 | 3 | 2.9 (4.8) | -3 | 0.4 | 5 | 4.8 (2.4) | -4 |
| Chlordane, alpha (373) | 10 | 9.6 (3.9) | -4 | 3 | 2.9 (4.0) | -3 | 0.4 | 5 | 4.6 (4.2) | -8 |
| Chlordane, gamma (373) | 10 | 9.6 (4.6) | -4 | 3 | 2.7 (4.8) | -10 | 0.4 | 5 | 4.4 (3.5) | -12 |
| 4,4'-DDD (235) | 10 | 10.4 (3.8) | +4 | 3 | 2.9 (3.8) | -3 | 0.4 | 5 | 4.8 (2.5) | -4 |
| 4,4'-DDE (246) | 10 | 9.8 (3.2) | -2 | 3 | 2.8 (5.4) | -7 | 0.5 | 5 | 4.5 (4.5) | -10 |
| 4,4'-DDT (235) | 10 | 10.9 (3.0) | +9 | 3 | 2.9 (4.5) | -3 | 0.4 | 5 | 4.7 (3.9) | -6 |
| Dieldrin (79) | 10 | 10.6 (3.2) | +6 | 3 | 2.9 (7.6) | -3 | 0.7 | 5 | 4.5 (4.3) | -10 |
| Endosulfan I (195) | 10 | 9.6 (5.8) | -4 | 3 | 3.1 (4.8) | +3 | 0.5 | 5 | 4.4 (5.0) | -12 |
| Endosulfan II (195) | 10 | 10.2 (4.5) | +2 | 3 | 3.3 (6.3) | +10 | 0.7 | 5 | 3.5 (4.1) | -30 |
| Endosulfan sulf. (272) | 10 | 10.6 (2.3) | +6 | 3 | 3.2 (4.4) | +7 | 0.4 | 5 | 4.8 (1.7) | -4 |
| Endrin (81) | 10 | 11.0 (2.8) | +10 | 3 | 3.6 (7.0) | +20 | 0.8 | 5 | 5.4 (7.5) | +8 |
| Endrin aldehyde (67) | 10 | 9.0 (9.8) | -10 | 3 | 2.8 (8.4) | -7 | 0.7 | 5 | 4.4 (4.8) | -12 |
| Endrin ketone (67) | 10 | 11.5 (0.61) | +15 | 3 | 3.2 (1.9) | +7 | 0.2 | 5 | 4.7 (3.0) | -6 |
| Heptachlor (272) | 10 | 10.6 (5.1) | +6 | 3 | 2.6 (5.3) | -13 | 0.4 | 5 | 4.9 (3.5) | -2 |
| Heptachlor epox. (353) | 10 | 10.0 (2.5) | 0 | 3 | 3.0 (5.9) | 0 | 0.6 | 5 | 4.8 (3.9) | -4 |
| Methoxychlor (227) | 10 | 11.4 (1.6) | +14 | 3 | 3.1 (2.3) | +3 | 0.2 | 5 | 4.8 (3.8) | -4 |
| Nonachlor, trans (409) | 10 | 9.5 (4.6) | -5 | 3 | 2.8 (2.4) | -7 | 0.2 | 5 | 4.4 (4.3) | -12 |
| All pesticides | 10 | 10.2 (7.1) | +2 | 3 | 2.9 (8.6) | -2 | | 5 | 4.6 (7.7) | -8 |

Table 15. (Cont.) Accuracy and Precision of Automated Measurements of PCBs and Pesticides in Fortified Water Extracts

| Analyte (Meas. Ion) | Medium Level Reagent Water[a] | | | Low Level Reagent Water[b] | | | | Ohio River Water[a] | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | True Conc. ug/L | Mean Meas. Conc., ug/L (RSD, %) | Mean Bias % | True Conc. ug/L | Mean Meas. Conc., ug/L (RSD, %) | Mean Bias % | Method Detect. Limit | True Conc. ug/L | Mean Meas. Conc., ug/L (RSD, %) | Mean Bias % |
| PCBs | 130 | 110 (2.9) | -15 | 27 | 21.2 (2.8) | -21 | c | 70 | 51.3 (2.5) | -27 |
| $Cl_1$ (188) | - | 3.6 (9.9) | - | | 0.7 (15) | - | | | 1.03 (4.8) | |
| $Cl_2$ (222) | - | 6.5 (5.7) | - | | 1.2 (10) | - | | | 3.42 (3.9) | |
| $Cl_3$ (256) | - | 17.2 (5.3) | - | | 3.1 (10) | - | | | 10.1 (3.0) | |
| $Cl_4$ (292) | - | 21.7 (4.1) | - | | 4.1 (3.8) | - | | | 11.0 (4.5) | |
| $Cl_5$ (326) | - | 28.8 (3.6) | - | | 5.6 (2.8) | - | | | 15.4 (3.6) | |
| $Cl_6$ (360) | - | 9.8 (5.7) | - | | 1.6 (3.1) | - | | | 4.86 (6.4) | |
| $Cl_7$ (394) | - | 1.3 (4.3) | - | | - - | - | | | 0.335(4.8) | |
| $Cl_8$ (428) | - | 7.1 (3.5) | - | | 1.6 (2.7) | - | | | 1.56 (4.3) | |
| $Cl_9$ (466) | - | 12.6 (5.3) | - | | 2.7 (4.6) | - | | | 3.00 (1.8) | |
| $Cl_{10}$ (500) | - | 2.0 (16.8) | - | | 0.6 (12) | - | | | 0.442 (1.8) | |
| Surrogate Compounds | | | | | | | | | | |
| $^{13}C_6$-gamma-BHC (187) | - | - - | - | 3 | 3.0 (3.4) | 0 | 0.3 | 5 | 4.9 (1.4) | -2 |
| $^{13}C_{12}$-4,4'-DDT (247) | - | - - | - | - | - - | - | - | 5 | 4.4 (7.0) | -12 |

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[a] Results of analysis of five replicate extracts of 1-L aliquots of fortified water.

[b] Results of analysis of seven replicate extracts of 1-L aliquots of fortified water.

[c] PCB method detection limits cannot be determined because Aroclor mixtures were used to fortify samples.

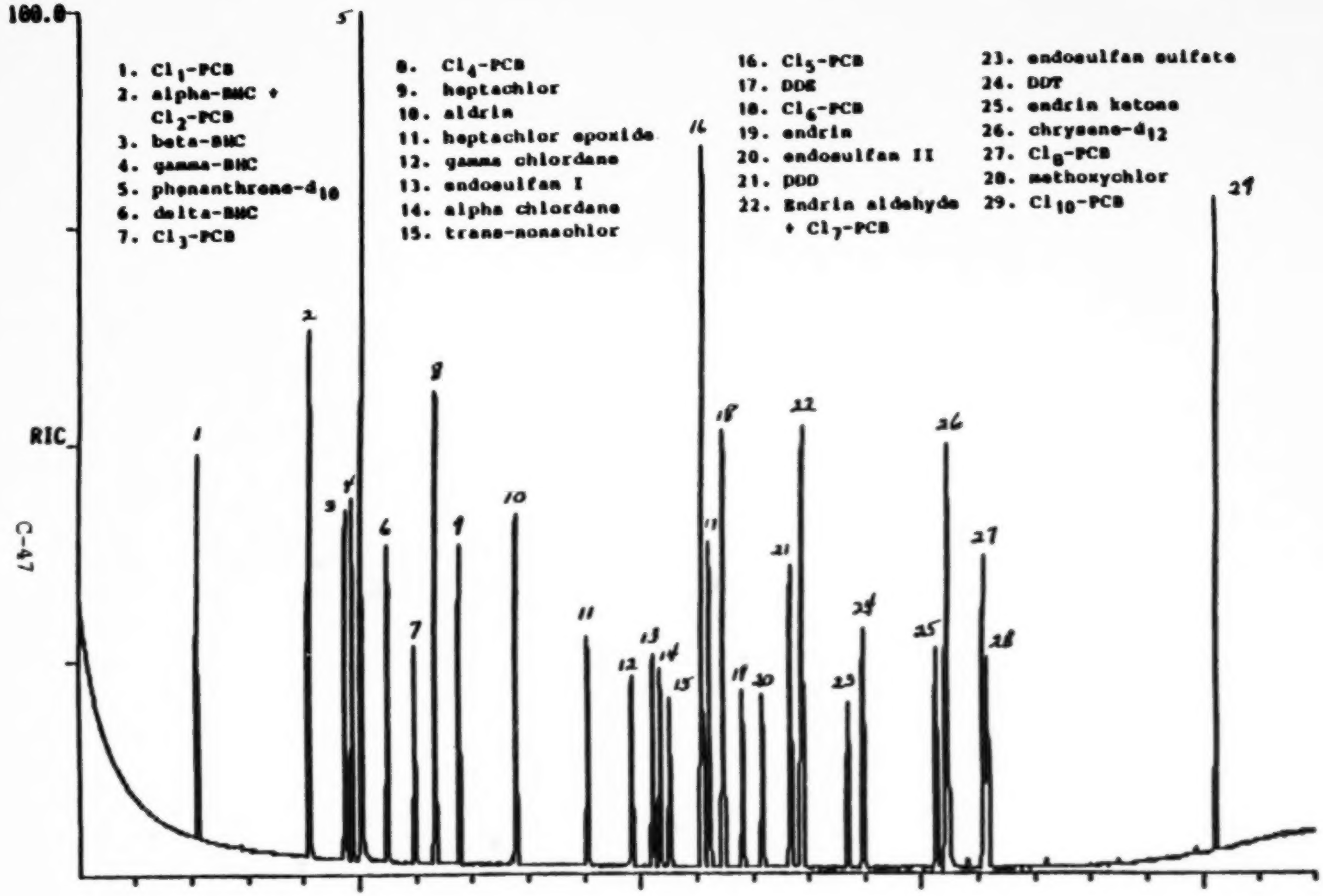

Figure 1. Total Ion Current Profile of PCB Calibration Congeners and Pesticide Analytes.

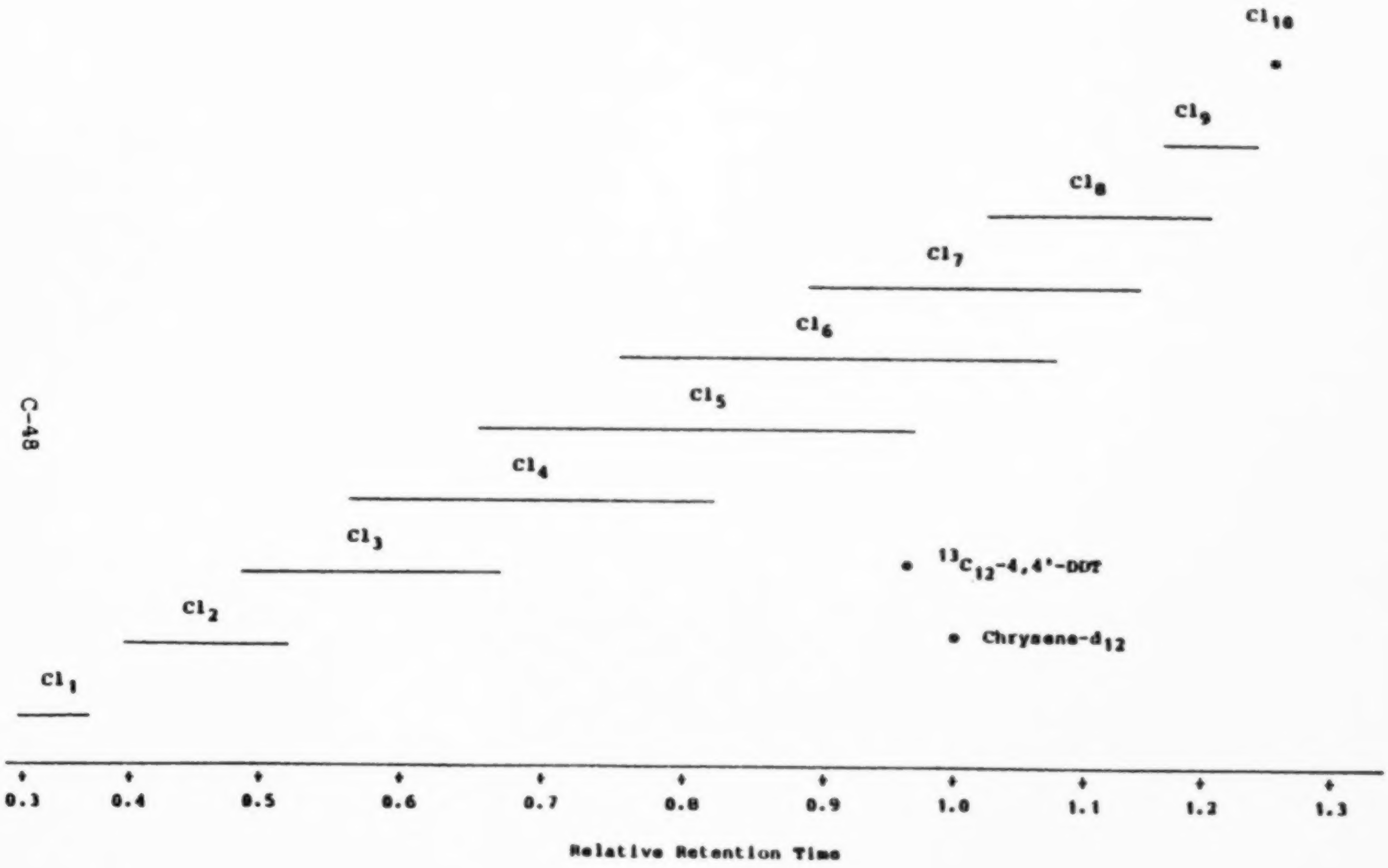

Figure 2. Diagram indicating approximate relative retention times (DB-5 GC column; chrysene-$d_{12}$ internal standard) of PCB isomer groups and retention time marker compounds (for PCB SIM data acquistion option).